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THE SOLUBILITY EQUILIBRIUM BETWEEN SILVER CHLORIDE, SILVER OXIDE, AND SOLUTIONS OF POTASSIUM CHLORIDE AND HYDROXIDE.

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THE theoretical application of the Mass-Action Law and the Ionic Theory to the type of equilibria to which the case named in the title belongs has already been made by Nernst,[1] who also interpreted the well-known results of Guldberg and Waage with barium carbonate and sulphate in accordance with the theory. The principle of the equilibrium is very simple; namely, since

$$C_{Ag^+} \times C_{Cl^-} = S^2_{AgCl}, \text{ and } C_{Ag^+} \times C_{OH^-} = S^2_{Ag_2O},$$

it follows that

$$C_{Cl^-}/C_{OH^-} = S^2_{AgCl}/S^2_{Ag_2O};$$

that is, that the ratio of the concentrations of the chlorine and hydroxyl ions in any solution which is simultaneously saturated with silver chloride and oxide is constant and equal to the ratio of the squares of the solubilities of these two salts in pure water, it being assumed that the two salts are completely dissociated. This principle is of importance not only because it underlies a frequently occurring type of chemical reaction, but also because it

[1] "Theoretische Chemie," Second edition, p. 498.

furnishes an indirect means of determining the solubility in water of salts which are so difficultly soluble that the concentration of their saturated solutions can not be directly determined by analytical methods. We have therefore thought it worthy of further investigation.

An experimental investigation of the analogous principle that applies in the case where one of the difficultly soluble salts is trionic has been made by Findlay,[1] who studied the equilibrium between lead sulphate, lead iodide, and solutions of sodium sulphate and iodide. The theory was found to be confirmed.

Our own investigation consisted in determinations of the solubility in water of silver oxide (and incidentally of silver iodate), and of the concentrations of solutions containing both potassium chloride and hydroxide that are in equilibrium simultaneously with silver chloride and oxide.

The substances used were prepared as follows: Silver oxide was made by precipitating silver nitrate solution with a clear solution of barium hydroxide, and the precipitate was washed by decantation with four liters of freshly boiled water and collected on a filter. The precipitation, washing, and filtration were carried out in an apparatus so arranged that the precipitate did not come at any time in contact with ordinary air containing carbon dioxide. Its purity was established by "rotating" successively the same portion of the oxide with fresh quantities of water, and determining the amount dissolved, which proved to be constant. Silver chloride was prepared by precipitating silver nitrate solution with hydrochloric acid and washing the precipitate thoroughly in a beaker protected from the light. A potassium hydroxide solution was made by dissolving commercial potassium hydroxide "from alcohol" in water, determining analytically the amount of carbonate present, adding the amount of barium hydroxide solution necessary to precipitate it, and decanting the solution after the precipitate had settled. This solution was found to give a faint test for carbonate upon adding more barium hydroxide; but, as it also gave a slight precipitate with sulphuric acid, it was evident that a quantity of barium substantially equivalent to the carbonate had been added. A potassium chloride solution was made from

[1] *Ztschr. phys. Chem.*, **34**, 409 (1900).

salt which had been precipitated by hydrochloric acid and ignited.

The solutions of the pure silver salts in water were saturated by rotating them in a thermostat at 25° for four or five hours in the apparatus described by Noyes.[1] The state of saturation was approached both from the undersaturated and from the supersaturated side. After allowing the solid particles to settle for a short time, the solutions were sucked out of the bottles, which were left standing in the thermostat, through a filter placed in a closed funnel into a 250 cc. graduated flask. The solutions were then precipitated with potassium iodide, about 0.5 cc. of a saturated barium nitrate solution being also added to promote the coagulation. The precipitates were collected in platinum Gooch crucibles upon a layer of finely divided platinum, dried at 160°, and weighed.

The results obtained with silver oxide and with silver iodate[2] are given below. The figures represent the grams of silver iodide obtained from 250 cc. of saturated solution.

TABLE I.

Silver oxide.		Silver iodate.	
From undersaturation.	From supersaturation.	From undersaturation.	From supersaturation.
0.0125	0.0127	0.0109	0.0112
0.0130	0.0120	0.0107	0.0113
0.0125	0.0133	0.0112	0.0117
0.0102[3]	0.0112[3]	0.0108	0.0106
.....	.....	0.0111	0.0114
0.0127	0.0127	0.01094	0.01124

It will be seen that the means of the "undersaturated" and "supersaturated" values agree completely in the case of the silver oxide, and fairly well in the case of the iodate.

The solubilities expressed in mols per liter corresponding to the final means are 2.16×10^{-4} for silver oxide, and 1.89×10^{-4} for silver iodate.

The solubility of the silver iodate was determined with the idea that it might prove a satisfactory salt to use in connection with silver oxide in testing the theory under consideration. But, since

[1] *Ztschr. phys. Chem.*, **9**, 606 (1892).

[2] The silver iodate was prepared by precipitating a solution of silver sulphate with one of potassium iodate made from the recrystallized salt. The precipitate was washed thoroughly with hot water.

[3] Omitted in the calculation of the mean.

the solubilities proved to be so nearly identical, and since therefore the ratio of them would not differ greatly from the ratio of their squares, it was decided to combine silver chloride with the silver oxide; and no further work was done with the iodate.

In the first series of experiments with mixed salts, an excess of moist silver oxide and chloride was added to an approximately 1/3 normal solution of potassium hydroxide, and the mixtures were rotated in the thermostat at 25° for a number of hours. In half of the experiments, the mixtures were heated above 25° and shaken, before placing them in the thermostat; but no systematic difference was shown by the results. After the rotation, the solutions were allowed to settle, filtered in the manner above described, and portions of 50 cc. and 200 cc. measured out. The 50 cc. portion was titrated with 0.5217 normal nitric acid[1] to determine the hydroxide present, and was then united with the 200 cc. portion. The whole was then acidified with nitric acid and precipitated with silver nitrate; the precipitated silver chloride was collected in Gooch crucibles, dried, and weighed.

The experimental results and the calculated ratio are given in the following table: The first column contains the number of the experiment; the second, the grams AgCl obtained from 250 cc. of saturated solution; the third, the cubic centimeters of 0.5217 normal HNO_3 neutralized by 50 cc. of saturated solution; the fourth and fifth, the corresponding number of millimols of KCl and KOH respectively per liter; and the sixth, the ratio $C_{Cl'}:C_{OH'}$, calculated in the manner described below.

TABLE II.

Expt. No.	AgCl. Gram.	HNO_3. Cc.	C_{KCl}.	C_{KOH}.	$C_{Cl'}/C_{OH'}$.
1.....	0.1181	31.60	3.295	329.7	0.01070
2.....	0.1184	32.10	3.303	334.9	0.01056
3.....	0.1231	34.30	3.434	357.8	0.01028
4.....	0.1269	34.35	3.540	358.3	0.01058
5.....	0.1256	34.20	3.503	356.8	0.01052
6.....	0.1222	33.50	3.410	349.5	0.01045
			Mean.....		0.01052

A second series of two experiments (Nos. 7 and 8) was made

[1] This had been standardized through a sodium hydroxide solution against a hydrochloric acid solution in which the acid had been determined by precipitation with silver nitrate.

in which a weaker potassium hydroxide solution (about 0.065 molar) was substituted for the stronger (one-third molar) solution. And in a third series, consisting of four experiments (Nos. 9-12), five times as much solid potassium chloride was added at the start to the potassium hydroxide solution as was present after equilibrium was reached. The results are given in the following table:

TABLE III.

Expt. No.	AgCl. Gram.	HNO_3. cc.	C_{KCl}.	C_{KOH}.	$C_{Cl'}/C_{OH'}$.
7.....	0.0239	6.78	0.666	70.7	0.00995
8.....	0.0190	5.72	0.530	59.7	0.00938
9.....	0.0177	5.20	0.494	54.2	0.00961
10.....	0.0222	6.23	0.620	65.0	0.01006
		Mean.....			0.00975
11.....	0.0375	10.50	1.046	109.5	0.01020
12.....	0.0329	9.05	0.918	94.4	0.01038
		Mean.....			0.01029

It will be seen that the values of the ratio $C_{Cl'}/C_{OH'}$ check fairly well in each set of experiments where the potassium hydroxide concentration was approximately the same. This is true especially of the values of Table II where that concentration and the weight of silver chloride obtained were the greatest. There is a slight decrease in the ratio (from 0.0105 to 0.0098) with decrease of concentration (from 0.35 to 0.06 molar KOH). This is, however, of a secondary magnitude, and the general agreement of the results obtained at different concentrations and by different methods of approaching the equilibrium-condition proves that there can be no considerable error in the results.

A few words must be added in regard to the manner of calculating this ratio. It consisted in first multiplying the concentrations of the two salts given in the fourth and fifth columns of the tables by their respective degrees of dissociation. These last were determined by the following method, which seems to us to be the most exact one for the calculation of the dissociation of salts, in the presence of each other, which do not follow the Mass-Action Law. It is based on the principle demonstrated by solubility experiments,[1] that the concentration of the undissociated part of

[1] See Noyes and Abbott: *Ztschr. phys. Chem.*, **16**, 138 (1895).

a salt has the same value, when the product of the concentrations of its ions has the same value, whatever may be the two separate factors of that product. This principle may be applied to the present case in the following manner. In the experiments in Table II the potassium chloride solution is about 0.0033 molar and the hydroxide solution about 0.35 molar. As a first rough approximation we may assume each salt to be 85 per cent. dissociated; and we then get for the product $C_{K^+} \times C_{Cl'}$, the approximate value, $(0.35 + 0.0033) \times 0.85 \times 0.0033 \times 0.85$. The square root of this quantity (or 0.030) is 85 per cent. of the concentration (0.0355) of pure potassium chloride at which the degree of dissociation is the same as it is in the solution of the mixed potassium salts. This degree of dissociation can then be ascertained by reference to a table, or better a plot, of molar-conductivity values. In this case with the help of the data of Kohlrausch and Maltby,[1] it is found to be 90 per cent. In a similar way the dissociation of the potassium hydroxide is found to be 84 per cent.[2] These values are used in calculating the ratios for all six experiments given in Table II. For experiments 7-10 in Table III, the dissociation of the chloride is found to be 95 per cent., and that of the hydroxide 90 per cent. For experiments 11 and 12, the corresponding values are found to be 94 and 88 per cent., respectively.

Adopting for the ratio the round value 0.0100, which is as accurate a conclusion as the experiments admit of, it follows from the equation given at the beginning of this article that the solubility of the chloride should be almost exactly one-tenth $(= \sqrt{0.01})$ of that of the oxide, or 2.16×10^{-5} mols per liter, adopting our analytically determined value for the oxide. The value found by Kohlrausch and Rose[3] by conductivity measurements at 25° was 1.50×10^{-5}. These two quantities are of the same order of magnitude, and to that extent they furnish a confirmation of the theory. Thus, if the fact of the electrolytic dissociation of the two silver salts was not taken into account, it might be expected that the ratio of the solubilities themselves, instead of that of their squares, would be equal to the ratio $C_{Cl'}/C_{OH'}$, and consequently

[1] *Sitzungsber. königl. preuss. Akad. der Wissenschaften*, (1899), p. 665; (1900), p. 1006.

[2] Assuming the limiting value $(\Lambda K + \Lambda OH')$ to be equal to 239 at 18° (Kohlrausch: *Sitzungsber.* just cited, (1901), p. 1031) and using also his data for the higher concentrations.

[3] *Ztschr. phys. Chem.*, **12**, 242 (1893).

that the solubility of silver chloride would be 0.216×10^{-5} —an enormous divergence from the result by the conductivity method. It is, nevertheless, true that the deviation of the solubility-ratio directly determined from that predicted from the equilibrium experiments is greater than can, with any degree of probability, be accounted for by the experimental errors, even though these may be considerable in the case of the solubilities of two such difficultly soluble salts. There is, moreover, one explanation of a theoretical nature that would account for the results; namely, the assumption, by no means *a priori* improbable, that silver hydroxide in saturated solution is not even approximately completely dissociated. If Kohlrausch and Rose's value for silver chloride be considered correct and by means of the ratio $C_{Cl'} : C_{OH'}$, the "solubility" of silver oxide be calculated from it, this is found to be 1.50×10^{-4}, while the analytically determined value is 2.16×10^{-4}. The former value which has been considered to be the solubility represents in reality, according to the theory, only the concentration of the dissociated portion in the saturated solution; and, admitting the accuracy of the data, the conclusion might be drawn from them that silver hydroxide in its saturated solution is 70 per cent. dissociated. No independent evidence can be cited, as far as we know, either for or against this conclusion. We have considered the possibility of verifying it by conductivity measurements; but, in view of the difficulties known to exist in the case of such very dilute solutions of bases, it has seemed to be hopeless to obtain sufficiently accurate results, at any rate unless extraordinary precautions were taken, and the matter were made the subject of an extended investigation.

The results of this investigation may be fully summarized as follows:

Solubility determinations at 25°, in which the ordinary methods of analysis were employed, gave for silver oxide 2.16×10^{-4} mols AgOH per liter, and for silver iodate 1.89×10^{-4} mols $AgIO_3$ per liter.

The ratio of the concentrations of the chlorine and hydroxyl ions in solutions of potassium chloride and hydroxide which are simultaneously saturated with silver chloride and oxide increases

only 8 per cent. with a sixfold multiplication of the concentrations of the former salts, and has very nearly the value, 0.0100.

Assuming that the two silver compounds are completely dissociated in their saturated solutions, the requirement of the Mass-Action Law and the Ionic Theory that the ratio of the squares of their solubilities be equal to the concentration-ratio just referred to, leads to the conclusion that the solubility of silver oxide in water is ten times that of silver chloride. The value for silver oxide determined directly by us is, however, 14.4 times that obtained for silver chloride by Kohlrausch and Rose by the conductivity method. It is pointed out that this divergence would be accounted for by the assumption that silver hydroxide in saturated solution is only 70 per cent. dissociated.

An exact method is described of deriving the dissociation of two dissolved salts in the presence of each other, which consists essentially in considering the dissociation of each salt to be that which conductivity measurements show it to have when it is alone present at a concentration of its ions equal to the square-root of the product of the concentrations of its ions in the solution of the mixed salts.

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SOME NOTES CONCERNING HALPHEN'S TEST FOR COTTONSEED OIL.

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SINCE Halphen's reaction for cottonseed oil was first published in 1897,[1] it has been submitted to more or less rigid test by a considerable number of investigators. Although some differences of opinion have arisen as to its merits and general applicability, it seems to have been quite generally accepted as the most reliable method at hand for detecting the presence of cottonseed oil in admixture with other oils or fats.

K. Mazher,[2] after using nitric acid, Hirschsohn's reagent, Becchi's test, and Halphen's reaction, concludes that only the latter is to be depended upon.

[1] *J. Pharm. Chim.*, **9**, 392 (1897).
[2] *Ibid.*, **17**, 159.

J. Wauters[1] reviewed the Becchi test at some length, and concluded that Halphen's reaction is more reliable. He found it to be very delicate, and reported his ability to detect, by its use, 0.25 per cent. of cottonseed oil in a mixture. He also found it possible to determine the approximate amounts of oil in a mixture by comparison with known mixtures. R. D. Oilar[2] gave it extended trial and found it to be reliable for 0.50-0.25 per cent., and that it was even possible to detect such small amounts as $^1/_{16}$ of 1 per cent. Raikow and Tscherweniwanow[3] found it to be sensitive to 0.50 per cent. Many others have found the test as proposed by Halphen to be very satisfactory, and it seems to have great favor among chemists at the present time.

There is, however, some lack of agreement as to its reliability in the case of old or rancid oils.

J. Wauters[4] claims that old oils also respond to the test. P. Soltsien[5] states that the age and rancidity of the oil have no influence upon the characteristic reaction. R. D. Oilar,[6] on the other hand, found that old and rancid oils do not produce the crimson coloration.

The object of this article is not to discuss the sensitiveness nor reliability of Halphen's reaction when applied to normal oils, but rather to call more special attention to two points in connection with its use which require some emphasis. It is manifest that the diagnostic value of the test must be dependent upon all the conditions which affect it. The first point to be considered is the effect of heat upon cottonseed oil in its relation to Halphen's reaction, and the effect of high temperatures upon the palatability of the oil. It is conceded that the substance in the oil to which the characteristic coloration is due, can be eliminated by heat. Whether it is volatilized unchanged, or whether it is decomposed by the heat, is immaterial.

Raikow[7] has shown that the active substances in Becchi's and Halphen's reactions are not identical, and that by oxidation with

[1] *Bull. Assoc. Belg. Chim.*, **10**, 404-416 (1899).
[2] *Am. Chem. J.*, **24**, 353-373.
[3] *Chem. Ztg.*, 1899, pp. 1025-1028.
[4] *Bull. Assoc. Belg. Chim.*, **10**, 404-416 (1899).
[5] *Ztschr. öffentl. Chem.*, **5**, 106-107.
[6] *Am. Chem. J.*, **24**, 355-373.
[7] *Chem. Ztg.*, 1900, pp. 562-563.

potassium permanganate an oil can be rendered inactive to the latter, while responding with undiminished intensity to the former. This would seem to indicate that the color-producing substance in Halphen's test is easily oxidizable, possibly aldehydic in character, although Gill and Dennison[1] were unable to detect the presence of bodies of this nature in cottonseed oil. But whatever may be the nature of this active substance, it cannot withstand high temperatures. Raikow and Tscherweniwanow[2] found that it was destroyed by heating with superheated steam, or at a temperature of 220° C.

Allen[3] states that oil heated to 245° C. still gives the Halphen reaction but with diminished intensity. Gill and Dennison[4] state, as the result of their own experiments, that when heated to 260° C., an oil will no longer respond to the test. P. Soltsien[5] observes that the reaction still takes place when oil is heated to 200° C., but that a temperature of 250° C. destroys its sensitiveness to the test. D. Holde and R. Pelgry[6] found that a temperature of 200°-210° C. served to lessen the intensity of the coloration produced, and that when oil is maintained at 250° C. for ten minutes, it is no longer capable of producing a color change.

R. D. Oilar[7] concludes from his experimental work that the temperature at which the oil is rendered inactive, depends upon the nature of the containing vessel, and duration of the heating. He found that in glass vessels a temperature of 315°-320° C. was necessary in order to destroy the capability of color reaction, but that the same result was produced by heating the oil for one hour in a steel frying pan, at 140°-150° C.

Some experiments recently carried out in our laboratory showed that a temperature of 265°-270° C. is necessary to render the oil *wholly* inactive. The results given below were obtained with a sample of cottonseed oil which had been sold upon the market for olive oil. It was yellow in color, and had an iodine number of 106.3. It was not in the slightest degree rancid. The tests were

[1] This Journal, **24**, 397-398 (1902).
[2] *Chem. Ztg.*, **23**, 1025-1028 (1899).
[3] "Commercial Organic Analysis," Vol. II, Part I, third edition, p. 143.
[4] This Journal, **24**, 397-398 (1902).
[5] *Ztschr. öffentl. Chem.*, **5**, 135-136.
[6] *Chem. Rev. Fett. u. Harz. Ind.*, **6**, (4) 67-68.
[7] *Am. Chem. J.*, **24**, 355-373.

applied as follows: Eight test-tubes were prepared, each containing 10 cc. of oil, 10 cc. of colorless amyl alcohol, and 10 cc. of carbon disulphide containing 2 per cent. of sulphur. In one tube unheated oil was used; in another, oil that had been previously heated to 180° C. for ten minutes; in the other tubes oil was used which had been heated ten minutes at the following temperatures: 200°, 210°, 220°, 240°, 260° and 280° C. The test-tubes and contents were heated in a bath of glycerol and water to 110° C. for fifteen minutes. Results as follows: The unheated oil gave a deep crimson coloration. That which had been previously heated to 180° C. gave a crimson coloration which was very perceptibly lighter than that given by the unheated oil. There was a gradual lessening of intensity of the color produced by the oil which had been heated to 200° and 210° C., while that which had been submitted to a temperature of 220° C. gave only a light crimson coloration; a slight pink color resulted from the sample heated to 240° C., and only a very faint tinge of pink from that heated to 260° C., while the contents of the tube containing the oil which had been previously heated to 280° C. showed no trace of color.

Soltsien[1] and others believe that cottonseed oil which has been heated to 250° C. is no longer fit for edible purposes. Our work, although by no means disproving this belief, seems to indicate that possibly it is erroneous. The oil was raised gradually to a temperature of 280° C. by us, by heating it in open test-tubes in a paraffin bath. It was kept at this temperature for ten minutes and the only observable difference between it and the unheated oil was an almost imperceptible deepening of the yellow color. At this date, three months after the heating, the heated and unheated samples show no difference in taste or odor. It is probable that oils produced by different methods of extraction and refining may be more or less dissimilar, and hence results from a single sample cannot be regarded as conclusive, although the presumption is strong in favor of the view that oils would differ but little in the characteristic just mentioned. It is, of course, superfluous to remark that if cottonseed oil can be heated to a temperature sufficient to destroy its color reaction without injuring its palatability, Halphen's test cannot be wholly reliable for detecting its presence

[1] *Zischr. öffentl. Chem.*, **5**, 135-136.

when mixed with other oils or fats. However, it is not necessary to completely destroy the capability of color production, and hence not necessary to heat the oil to 265°-270° C., in order to render the test untrustworthy. Heating to 220°-230° C. would be sufficient. This fact brings us to the second point to be emphasized; *viz.*, that the active substance in cottonseed oil to which the characteristic coloration in Halphen's reaction is due, is transmitted apparently unchanged into the fat of animals fed on cottonseed meal.

J. Wauters[1] says that when Halphen's test is applied to butter from cows fed on cottonseed meal, a coloration is obtained equivalent to about 1 per cent. of cottonseed oil. F. Werenskiold[2] is responsible for the assertion that when cows were fed 1 kilo per day of peanut cake, no test for arachidic acid could be obtained in the butter they produced; but that when an equal amount of cottonseed meal was fed, the butter gave a distinct reaction for cottonseed oil with Halphen's reagent.

Allen[3] states that lard and lard oil obtained from animals which have been fed on cottonseed meal, will often respond faintly to Halphen's test. The same statement is repeated by Leffmann and Beam.[4] P. Soltsien[5] stated that he had met with American lards which gave a very weak reaction with Halphen's test, equivalent to about 1 per cent. of cottonseed oil. The same authority reported at a later date[6] that he had obtained a color reaction, also with American lards, equivalent to that given by a mixture containing 25 per cent. of cottonseed oil. The lards in question were obtained by a member of the German Consulate at Chicago, at Armour & Co's establishment, from hogs which had been liberally fed on cottonseed meal. This most astounding result reported by Soltsien has not been corroborated by any other worker. If correct, it almost shakes one's belief in animal metabolism.

In order to satisfy ourselves as to the accuracy of the several statements above quoted, a series of feeding experiments were planned by us so that samples of lard might be obtained from hogs

[1] *Bull. Assoc. Belg. Chim.*, **10**, 404-416 (1899).
[2] *Jahresber. öffentl. Veranstalt. Förd. Landw. Norwegen 1. J.*, 1897.
[3] "Commercial Organic Analysis," Vol. III, Part I, third edition, p. 143.
[4] "Food Analysis," p. 169.
[5] *Ztschr. öffentl. Chem.*, **7**, 25.
[6] *Ibid.*, **7**, 140 (1901).

which had received varying amounts of cottonseed meal as a part of their daily rations. Before we were ready to begin these, it was learned that Director John Fields, of the Oklahoma Experiment Station, was already engaged in a feeding experiment with cottonseed meal, and his cooperation was therefore solicited and secured. The samples of lard mentioned below were rendered from the fat of the hogs he was using in the feeding test, the following details of which were furnished by him. Our thanks are due Director Field for his cooperation. Four lots of hogs were used, each lot containing six animals. All of them had been fed uniformly before the beginning of the experiment, and all of them had received small amounts of cottonsed meal in their ration. The feeding experiment covered a period of fifty-six days, during which time the following rations were eaten:

Lot No. 1.	Lot No. 3.
2026 lbs. wheat chop.	$135\frac{1}{15}$ lbs. cottonseed meal.
Lot No. 2.	$1890\frac{14}{15}$ lbs. wheat chop.
$675\frac{1}{3}$ lbs. wheat chop.	Lot No. 4.
$337\frac{2}{3}$ lbs. wheat bran.	$66\frac{1}{6}$ lbs. cottonseed meal.
1013 lbs. wheat middlings.	$1928\frac{1}{3}$ lbs. wheat chop.

When the animals were slaughtered, a piece of fat about two inches square was taken from each one. Some of the pieces were taken from the head, and some from other portions of the body, but no leaf fat was included. The samples taken from the animals belonging to each lot were mixed and rendered, and the resulting lard sent to us. These lard samples were received and work upon them completed, before receiving any information concerning the rations fed to each lot, and hence our observations were free from any unconscious bias that might have resulted had such information been at hand. The results of our tests are as follows:

	Lot No. 1. Lab. No. 893.	Lot No. 2. Lab. No. 894.	Lot No. 3. Lab. No. 895.	Lot No. 4. Lab. No. 896.
Becchi's test	No reduction	Very slight reduction	Slight reduction	Very slight reduction
Halphen's test	Faint pink	Pink	Light crimson	Light pink
Approximate amount cottonseed oil[1]	1.2%	2.8%	4.0%	2.0%
Iodine number	55.48	59.96	52.96	53.03
Maumené's test: Rise in temp.	25.9°	25.7°	23.5°	26.0°
Maumené's test: Sp. temp. reaction[2]	0.64	0.63	0.58	0.64

[1] Obtained by comparison with known mixtures. [2] Rise in temperature of water, 40.5°.

The cottonseed oil used in the known mixtures for comparison, was the same as previously mentioned. Check tests were made upon lard from animals which had never been fed cottonseed meal, and in no case was the slightest coloration manifested.

These results confirm the observations of others that cottonseed meal will impart the characteristic color-producing power of the corresponding oil, to the fat of animals which eat it. They show a more decided reaction with Halphen's test than indicated by Allen, Wauters, and other authorities quoted, but are very far from corroborating the recent statement of Soltsien. They further show that the color-producing power of the cottonseed oil is very persistent when once introduced into the fat of an animal. Lots 1 and 2 had received no cottonseed meal in their ration for fifty-six days, and yet the lard from their fat showed a coloration with Halphen's reagent equivalent to 1.2 per cent. and 2.8 per cent. of cottonseed oil, lot No. 2 showing even a greater coloration than lot No. 4 which had eaten $66^1/_6$ pounds of cottonseed meal during the feeding period.

We propose carrying on, as soon as practicable, the feeding experiments originally planned, in order to continue our study of the effect of feeding cottonseed meal, upon lard in its relation to Halphen's test.

Summarizing the points above emphasized we have the following:

First.—Cottonseed oil is rendered inactive toward Halphen's reagent by heating to 260°-270° C.

Second.—The intensity of the reaction is very greatly diminished by heating the oil to 220°-240° C.

Third.—It is possible that cottonseed oil may be heated to 280° C. without injuring it, and reasonably certain that a temperature of 220°-240° C. will not render it unfit for use as an article of food, either alone, or as part of a mixture.

Fourth.—Lard from animals fed on cottonseed meal may respond to Halphen's reagent with an intensity of coloration equivalent to several per cent. of unheated cottonseed oil.

It naturally follows from these facts that a mixture of fats or oils may be prepared containing at least 25 per cent. of cottonseed oil which has been heated to 220°-240° C., or a much larger per-

centage if heated to 250°-260° C., which will give a coloration with Halphen's reagent not more intense than that obtained with lard from cottonseed meal-fed hogs. Under such conditions the value of the test for diagnostic purposes is somewhat questionable, especially in its application to the analysis of lard. It is claimed by lard manufacturers and cottonseed oil refiners that the oil is never heated to such a high temperature. This may be true, but it is nevertheless desirable that chemists should be on their guard, and not place too much reliance upon this comparatively new test. For normal, unheated oil, its value is unquestioned; but in view of the facts above discussed, its limitations should not be overlooked.

The analytical work in this paper was performed by Mr. R. W. Thatcher, assistant chemist of the Washington Experiment Station, to whom our thanks are due.

FIXATION OF ATMOSPHERIC NITROGEN BY ALFALFA ON ORDINARY PRAIRIE SOIL UNDER VARIOUS TREATMENTS.[1]

By Cyril G. Hopkins.

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Many different farmers have tried to grow alfalfa in various sections of Illinois and adjoining states, but, in most cases, it has been pronounced a failure. Where alfalfa has been grown with success in Illinois, it has usually been necessary to sow it on very rich ground or to keep it well manured.

In theory, alfalfa ought to grow and do well on these prairie soils, and it ought not to require heavy and frequent applications of manures, because alfalfa is a very deep rooting crop and is thus capable of drawing upon the soil to great depths for the necessary mineral elements of plant food, and, being a leguminous plant, it has the power of "gathering" nitrogen from the inexhaustible supply of the air, by means of bacteria which inhabit its roots.

Numerous observations made on several fields of alfalfa in different sections of the country during the past few years led the

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writer to question whether alfalfa has the power to secure nitrogen from the atmosphere, when grown on these prairie soils. First, because, in nearly every field examined, the plants presented the same peculiar appearance which plants show when grown under artificial conditions *with an insufficient supply of nitrogen.* Second, because, in none of the fields where alfalfa presented this appearance could there be found any tubercles, or nodules, upon the roots of the alfalfa. Third, because liberal applications of barnyard manure produced a vigorous growth and a natural and healthy appearance.

In order to investigate the question, why Illinois soil does not more generally produce good crops of alfalfa, a series of experiments was begun about a year ago. These experiments comprehended the application of various elements of fertility to ordinary black prairie soil, both singly and in combinations, and both with and without the inoculation of the soil with the alfalfa bacteria; that is, with the bacteria which are known to live upon the alfalfa root in other sections of the country. These experiments have been carried on in the pot culture laboratory under controlled conditions and also on plots of ground under field conditions.

POT CULTURE EXPERIMENTS.

The pot culture experiments were planned with a twofold object; first, to test the effect of applying different elements of plant food to the soil to determine the value of such applications for the growing of alfalfa, and, second, to determine the effect upon the growth of alfalfa of inoculating the soil with the bacteria which are able to live upon the roots of alfalfa and gather nitrogen from the air for use of the growing plant.

Applications of Different Elements of Plant Food.

These pot cultures comprise a double set of our regular series of experiments adopted for investigating soils by pot cultures, which is as follows:

Twelve pots are all filled with the soil to be investigated and they are then treated with the following applications:

Pot No. 1—Check. (Nothing applied).
Pot No. 2—Lime.
Pot No. 3—Lime and nitrogen.

Pot No. 4—Lime and phosphorus.
Pot No. 5—Lime and potassium.
Pot No. 6—Lime, nitrogen and phosphorus.
Pot No. 7—Lime, nitrogen and potassium.
Pot No. 8—Lime, phosphorus and potassium.
Pot No. 9—Lime, nitrogen, phosphorus and potassium.
Pot No. 10—Nitrogen, phosphorus and potassium.
Pot No. 11—Check.
Pot No. 12—Check.

The first ten pots really make the complete series. Pots 11 and 12 are extras, or additional checks.

There is a double trial as to the value of an application of lime. First, by comparison between 1 and 2, which shows the effect of applying lime alone. Second, by comparison between 9 and 10, which shows the effect of applying lime after insuring a sufficient supply of each of the elements, nitrogen, phosphorus, and potassium.

Pots 3, 4, 5, 6, 7, 8 and 9 will show the effect of applying to the soil, nitrogen, phosphorus, and potassium, singly and in all possible combinations, and in all cases, after a sufficient quantity of lime has been added to neutralize acidity.

In the following tables and in the photographs, 0 (zero) means no fertilizer; L means lime; N means nitrogen; P means phosphorus; K means potassium (kalium).

Inoculation with Alfalfa Bacteria.

As stated above, two series of pot cultures were made with alfalfa, each of which received the applications of the different elements of plant food as described above. One of these two series of twelve pots each was inoculated[1] with the alfalfa bacteria; the other series was not. In all other respects the two series were treated exactly alike. All of the pots were filled with ordinary Illinois, black, prairie soil, and twenty-five alfalfa seeds were planted in each pot. They were kept in the glass house and were watered with very clear rain-water which was practically free from nitrogen, but which contained a trace of lime dissolved from a new cistern in which it was stored.

[1] The inoculating solution was made by shaking 500 grams of soil (obtained from an old alfalfa field in Kansas) with 1000 cc. of water, and allowing it to settle for a few minutes. One cc. of the liquid was used for each alfalfa seed planted.

The pots were all planted in June, 1901. The seeds germinated quite well and a fairly uniform stand was secured in all of the pots. The small plants grew slowly and the different pots showed no very marked differences for several months. A small crop was cut from all the pots in the fall, but they all seemed very much alike and no weights of the cuttings were taken. During the winter the pots[1] showed some marked differences in the growth of the alfalfa and the weights of the cuttings of each pot were taken on March 14, 1902, but they are not reported in this paper.

Another crop was cut from all of the pots on April 23rd and the weights of the alfalfa secured from each pot are given in Table I.

TABLE I.—ALFALFA POT CULTURES; CUT APRIL 23, 1902. WEIGHTS IN GRAMS PER POT AND POUNDS PER ACRE.

Serial No.	Pot No.	Treatment applied.	Green alfalfa. Grams per pot.	Air-dry hay. Grams per pot.	Air-dry hay. Pounds per acre.
1	25	o :	9	2	320
1	37	o : Bacteria	37	9	1440
2	26	L :	12	2	320
2	38	L : Bacteria	34	7	1120
3	27	LN :	38	9	1440
3	39	LN : Bacteria	44	10	1600
4	28	LP :	7	1	160
4	40	LP : Bacteria	44	10	1600
5	29	LK :	7	1	160
5	41	LK : Bacteria	32	7	1120
6	30	LNP :	66	16	2560
6	42	LNP : Bacteria	79	19	3040
7	31	LNK :	55	11	1760
7	43	LNK : Bacteria	59	13	2080
8	32	LPK :	7	1	160
8	44	LPK : Bacteria	67	17	2720
9	33	LNPK :	65	16	2560
9	45	LNPK : Bacteria	85	22	3520
10	34	NPK :	68	16½	2640
10	46	NPK : Bacteria	100	20	3200
11	35	o :	10	2	320
11	47	o : Bacteria	24	5	800
12	36	o :	10	2	320
12	48	o : Bacteria	34	7	1120

[1] The pots used were 10.5 inches in diameter, so that one gram of produce per pot corresponds to one pound per square rod or to 160 pounds per acre. While the exact yield per pot is given in grams in the tabular statement, the computed rate of yield in pounds per acre is also given and this rate of yield is used in the discussion in the text. This is relatively accurate and it is used because we are accustomed to the basis of pounds per acre. Another advantage is that the results from the pot cultures thus become more easily comparable with the actual field results which are given in the following pages.

Effect of Inoculation.

The seven uninoculated pots receiving no nitrogen made comparatively small growth[1] and showed uniformly throughout the period of nearly six weeks the characteristic pale yellowish green color indicative of an insufficient supply of nitrogen. The yields from these seven pots are very small, in no case exceeding the rate of 320 pounds per acre, while 1650 pounds per acre is the average yield of the corresponding inoculated pots. The yield from the inoculated pots ranges from two and a half to seventeen times the yield from the uninoculated pots. For example, the most favored pot receiving no nitrogen (serial No. 8), to which applications of lime, phosphorus, and potassium were made, yielded, when uninoculated, only 160 pounds of hay per acre, while 2,720 pounds per acre was the yield of the corresponding inoculated pot.

The crops produced on the seven uninoculated pots receiving no nitrogen would certainly be pronounced a failure, but the inoculated pots which produced yields from 0.75 to 1.75 tons of alfalfa hay per acre in less than six weeks from the previous cutting give evidence of being a very decided success, considering that this is the third cutting and corresponds to the third clipping in the field, which is frequently too light to pay for saving.

Effect of Nitrogen and Bacteria.

The applications of nitrogen produced a very marked increase in yields, but it is interesting to note that even these artificial supplies of nitrogen had evidently become somewhat depleted by the removal of the previous crops and were no longer sufficient for the greatest possible growth of the alfalfa; and, consequently, in every case where pots receiving nitrogen were also inoculated, a notable increase in growth and yield occurred. In the most favored pots (serial No. 9), to which lime, phosphorus, and potassium were supplied with the nitrogen, this increased yield produced by the bacteria amounted to nearly one-half ton per acre, the uninoculated pot yielding at the rate of 2,560 pounds per acre, while 3,520

[1] It may be observed that the uninoculated pots receiving phosphorus or potassium, or both, with lime, but without nitrogen (4, 5, 8) yielded even less than the uninoculated pots which received lime only or no treatment whatever (1, 2, 11, 12). I know of no explanation for this unless it be found in the fact that the yield of the previous crops from these fertilized pots was larger than from the unfertilized pots and the supply of available nitrogen had been correspondingly reduced.

pounds was the rate of yield of the corresponding inoculated pot.

Effect of Phosphorus.

Applications of phosphorus (or potassium) without bacteria or nitrogen (4, 5, 8) are of no value to the alfalfa.

Phosphorus applied to the inoculated pots or to the uninoculated pots receiving nitrogen produced a very marked increase in yield in every instance. These results confirm the indications observed in the previous crops and prove conclusively that, after provision has been made for a sufficient supply of nitrogen, applications of phosphorus to this soil were greatly to the advantage of the alfalfa crop. For instance where lime and nitrogen alone were applied (3) 1,440 pounds of hay per acre were produced, while 2,560 pounds was the rate of yield where phosphorus was added (6). The treatment: lime, nitrogen, bacteria (3), produced a yield of 1,600 pounds, which was increased to 3,040 pounds by the addition of phosphorus (6). Under the most favorable conditions without phosphorus; that is, with lime, nitrogen, and potassium (7), the yields in pounds per acre were 1,760 and 2,080 without and with bacteria, respectively, and these yields were increased to 2,560 and 3,520 respectively, by the addition of phosphorus (9). The inoculated pot receiving lime and potassium (5) yielded at the rate of 1,120 pounds per acre, but, where phosphorus was added to this combination (8), the yield became 2,720 pounds.

Effect of Potassium.

Applications of the element potassium produced a slight increase in yield when added after sufficient nitrogen was provided (3, 7), but the increase becomes more marked when the potassium is added after both nitrogen and phosphorus have been supplied. For example, with both lime and phosphorus added, and nitrogen accumulated by the alfalfa bacteria, the yield was 1,600 pounds without potassium (4) and 2,720 pounds with potassium (8); and, when an inoculated pot was also given an application of nitrogen (6), it yielded at the rate of 3,040 pounds without potassium and 3,520 pounds with potassium.

It should be remembered that no conclusions can be drawn as to the relative value of applying lime to the soil used because of the

fact that the water used in all of the pots contained a trace of lime.

There is evidence that both phosphorus and potassium have an indirect value aside from their direct value as plant food for the alfalfa. This is the value of these elements to the bacteria. Bacteria themselves are living plants, and while they are microscopic in size they are almost infinite in number, and their multiplication and development are largely dependent upon the supply of available mineral elements of plant food. It will be observed that a yield of 2,080 pounds per acre (7) was secured without the addition of phosphorus. The yield became 3,520 pounds when phosphorus was applied (9). This increase of 1,440 pounds per acre may be due in part to the direct value of the phosphorus to the alfalfa and in part to its value in promoting the development of the bacteria and thus increasing the supply of nitrogen which the bacteria secure from the air and furnish to the growing alfalfa. Again, the addition of phosphorus to the combination, lime, potassium, bacteria, increased the yield from 1,120 (5) to 2,720 (8), an increase of 1,600 pounds per acre. The fact that the soil itself contained sufficient phosphorus to produce a yield of 2,080 pounds (7) tends to prove that the first 960 pounds of this 1,600 pounds' increase was due to the increased development of the bacteria resulting from the additional supply of available phosphorus; the remainder of the increase, 640 pounds, is probably due to both the direct and the indirect value of the phosphorus.

Without addition of potassium the maximum yield was 3,040 pounds (6); consequently the increase in yield from 1,600 pounds (4) to 2,720 pounds (8), resulting from the addition of potassium to the combination, lime, phosphorus, bacteria, was probably largely due to the increased development of the bacteria in the presence of a larger supply of available potassium.

The field experiments, which are described further on, give abundant evidence of the value of applications of lime in promoting the development of the alfalfa bacteria.

The photographic reproduction of the six pots receiving no artificial fertilizer, three of which were inoculated and three uninoculated, as they appeared on May 11th, less than three weeks after cutting off the crops discussed above, may be of interest (see Fig. 1).

Cuttings made from these six pots on May 21st just four weeks after the previous cuttings, gave the results shown in Table II.

TABLE II.—ALFALFA POT CULTURES; CUT MAY 21, 1902. WEIGHTS IN GRAMS PER POT AND POUNDS PER ACRE.

Serial No.	Pot No.	Treatment applied.	Green alfalfa. Grams per pot.	Air-dry hay. Grams per pot.	Air-dry hay. Pounds per acre.
I	25	0 :	7	I	160
I	37	0 : Bacteria	42	12	1920
II	35	0 :	8	2	320
II	47	0 : Bacteria	33	8	1280
12	36	0 :	6	2	320
12	48	0 : Bacteria	33	10	1600

It will be observed that the highest yield of the three uninoculated pots was 320 pounds per acre, while the average yield of the three inoculated pots was 1,600 pounds,—five times as great. These results only serve to confirm those secured from the preceding crops, and to show the value of the inoculation in a most conclusive manner.

When we remember that the twenty-four pots used in this series of experiments were all filled with the same kind of well-mixed soil, and that this soil is fairly representative of thousands of square miles of black prairie land in Illinois and adjoining states, that both series, of twelve pots each, were kept on the same table in the greenhouse, watered at the same times with exactly the same kind of water, and in every way treated exactly alike, except that one series was inoculated with alfalfa bacteria while the other series was not inoculated, then these most positive and conclusive results, as shown by the records of the experiment, including the color of the foliage, the height of the growing plants, the photographic reproductions, and the absolute yields per pot and rate of yield per acre, seem truly remarkable and appear to be of tremendous importance in solving the question, Why is alfalfa so commonly an unsuccessful crop on ordinary prairie soils?

FIELD EXPERIMENTS WITH ALFALFA.

An acre of ordinary slightly rolling black prairie land, capable of yielding 70 bushels of corn to the acre, was seeded with alfalfa in June, 1901. The soil was considerably better than ordinary cultivated soil (such as was used in the pot culture experiments).

Fig. 1.—Alfalfa pot cultures, showing effect of inoculating ordinary black prairie soil with alfalfa bacteria.

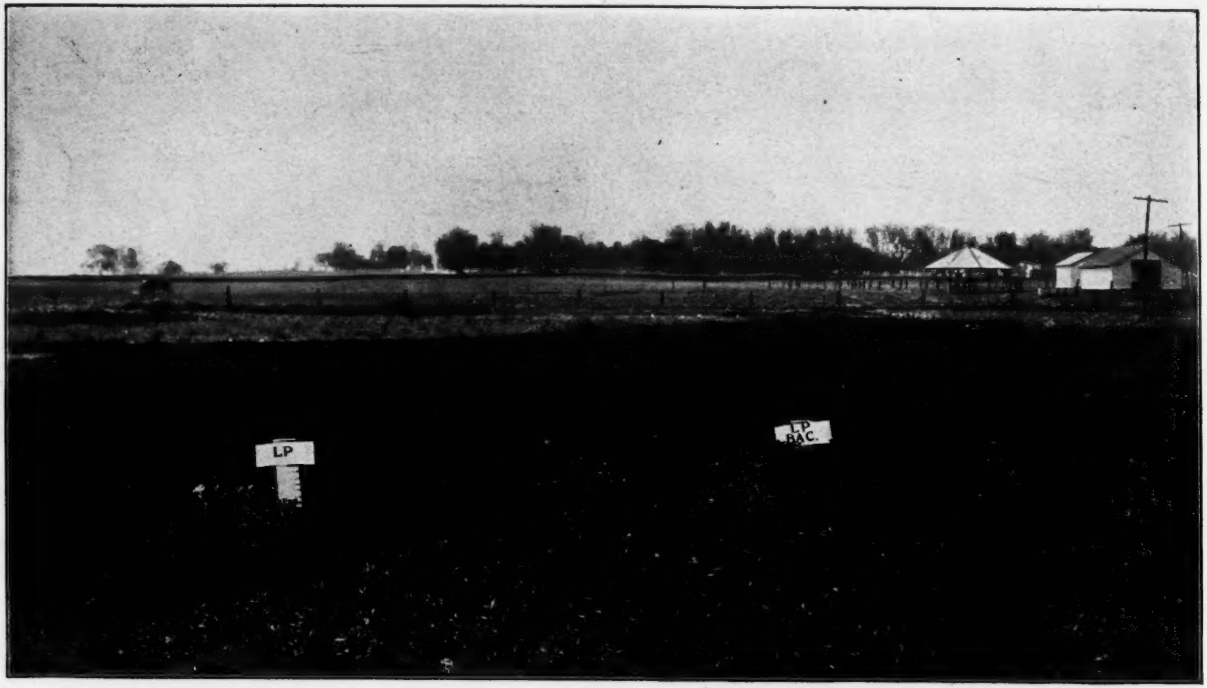


Fig. 2.—Alfalfa field experiments, showing effect of inoculating prairie soil after application of lime and phosphorus.

Previous to 1895, it had been in pasture for at least eighteen years, and since 1897 it had been in meadow; thus, only three grain crops (corn in 1895, 1896, and 1897) were grown on this soil during the past twenty-five years. The field, which was 8 rods wide east and west, and 20 rods long north and south, exclusive of some border and division strips, was divided into two parts by a line running north and south, and into five parts by lines running east and west. The west part of the acre was inoculated with soil taken from an old alfalfa field in Kansas. The five divisions from north to south were fertilized as follows:

Plot No. 1—Check (nothing applied).
Plot No. 2—Lime.
Plot No. 3—Lime and phosphorus.
Plot No. 4—Lime and potassium.
Plot No. 5—Lime, phosphorus, and potassium.

The rates applied per acre were: 320 pounds of air-slaked lime, 320 pounds of bone-meal (containing 30 per cent. phosphoric oxide), and 160 pounds of crude potassium sulphate.

The infected alfalfa soil was applied at different rates of seeding on narrow strips running north and south on the west half of the field, the lightest application (320 pounds) being on the west side, and, on successive strips eastward, the rates of application were 640, 960, 1,280, 1,600, and 1,920 pounds, respectively. Each of these strips was about one-half rod wide. A good stand of young plants was secured, but a very heavy rain storm, which occurred on July 2nd, washed the soil somewhat, and, as the west side of the field was somewhat higher than the east side, it was feared that the bacteria might be carried over the east plots and thus inoculate the whole field to some extent, which afterward proved to be the case, particularly along the east side where the water stood for a short time. The southeast quarter of the field was the lowest part, and, although it was tile-drained, the water stood on it long enough to kill most of the alfalfa plants. Because of these occurrences, the results of the experiment are probably not so marked as they would otherwise have been.

During the summer of 1901, the alfalfa was clipped three times, the clippings being left lying on the field. During midsummer, the weeds seemed to grow faster than the alfalfa, but with each

clipping the alfalfa improved, and in the fall the stand was good where it had not been injured by the water standing on it.

No marked differences were noted among the different plots, excepting that the alfalfa made a much more vigorous growth wherever phosphorus had been applied, the line being very noticeable where the application of phosphorus began.

In the fall, tubercles were found in abundance upon the plants growing in the strips of land where the heaviest applications of infected soil were made, but none were found on plants in the uninoculated soil.

In the spring of 1902 the alfalfa began to grow vigorously and was entirely free from weeds, but within a short time some very marked differences appeared among the different plots. The effect of the inoculation became very apparent, all of the inoculated soil producing a much more vigorous growth than occurred on uninoculated soil, and the more vigorous growth was accompanied by a dark green, healthy-looking color in the growing alfalfa, while the plants on uninoculated soil took on a pale green color indicative of an insufficient supply of nitrogen. This difference in growth and color between inoculated and uninoculated plants was very marked even where no fertilizer was applied, but it was more marked where lime was applied and still more marked where both lime and phosphorus were applied.

Fig. 2 shows the effect of inoculating soil to which both lime and phosphorus had been applied, the inoculated soil producing a markedly increased growth of alfalfa over the uninoculated soil. The label stakes are *two feet* high and serve as a measure of the height of the alfalfa. The difference in thickness of stand can be seen but the difference in color between the inoculated and uninoculated alfalfa is not brought out in the figure. To the southeast may be seen the patch of ground where the alfalfa was destroyed by water, on account of which no results were secured from plots 4 and 5.

Table III gives the yield per acre of air-dry hay from one-thousandth acre plots, the inoculated plots being measured off on the strip where the heaviest application of infected soil was made.

It will be seen that the inoculated plots yielded about twice as much hay as the uninoculated plots.

TABLE III.—ALFALFA FIELD EXPERIMENTS; FIRST CUTTING 1902, MAY 28. WEIGHT IN POUNDS PER PLOT AND PER ACRE.

Plot No.	Treatment applied.	Green alfalfa. Pounds per plot.	Air-dry hay Pounds per plot.	Air-dry hay. Pounds per acre.
1	O :	5½	1 5/16	1313
1	O : Bacteria	11	2 9/16	2563
2	L :	6	1 7/16	1438
2	L : Bacteria	12	2⅞	2875
3	LP :	7¼	1 13/16	1938
3	LP : Bacteria	15	3⅝	3625

QUANTITATIVE DETERMINATIONS OF THE FIXATION OF ATMOSPHERIC NITROGEN BY ALFALFA WHEN GROWN ON ORDINARY SOIL.

The investigations of Atwater in America, Boussingault and Ville in France, Hellriegel, Willfarth, and Nobbe in Germany, Lawes and Gilbert in England, et al., have fully established the scientific facts: (1) that leguminous plants, as the clovers, peas, beans, vetches, alfalfa, etc., have the power to gather, or accumulate, free nitrogen from the atmosphere; (2) that this fixation of free nitrogen is actually accomplished by microscopic organisms called bacteria which live in little nodules, or tubercles, upon the roots of the legumes; and (3) that, for different species of leguminous plants, there are also different species of "nitrogen-gathering" bacteria. Many investigations have also been conducted to determine the amounts of nitrogen which can be fixed by different leguminous plants, but these experiments have actually been carried on in pure sand cultures under conditions which necessitate that all nitrogen which the legume secures *must* be obtained from the air.

There is abundance of evidence that leguminous plants secure some nitrogen from the air when grown in ordinary soil, if they are provided with the bacteria. Indeed, the presence of the tubercles upon the roots is one of the evidences that free nitrogen is being fixed, and another evidence of that fact is found in the beneficial effects of clover and other legumes in crop rotations. It is a simple matter to determine how much nitrogen is contained in a ton of clover; but, after the amount is determined, it still remains a question as to how much of the nitrogen was taken directly from the soil and how much was secured from the air, and a question very frequently asked is, How much of their nitrogen do legumi-

nous crops obtain from the air and how much do they actually take from the soil?

The pot culture and field experiments described in the preceding pages were conducted on ordinary soil and in such a manner that it can be determined with a high degree of accuracy how much nitrogen was secured from the air by the alfalfa. This is due to the fact that, in all cases, alfalfa was grown not only with bacteria present but also in exactly similar duplicate pots or plots with bacteria absent and the difference between the amounts of nitrogen contained in the crop from the inoculated soil, on the one hand, and in the crop from the uninoculated soil, on the other hand, represents the amount of nitrogen which was secured from the atmosphere by the bacteria. Probably in no case will this amount be larger than the actual truth[1]; but, if the soil which was not intentionally inoculated had nevertheless to some extent become infected with alfalfa bacteria by cross inoculation, then the amount of nitrogen actually secured from the air would be even larger than represented by these determinations.

Fixation of Nitrogen by Pot Cultures.

Table IV gives in pounds per acre the amounts of dry matter and of nitrogen in the crops cut from the pot cultures on April 23, 1902; also the percentage of nitrogen in the dry matter and the

TABLE IV.—FIXATION OF NITROGEN BY ALFALFA IN POT CULTURES; CROPS CUT APRIL 23, 1902.

Serial No	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
1	25	0 :	280	2.61	7.31	....
1	37	0 : Bacteria	1300	4.09	53.17	45.86
2	26	L :	280	3.47	9.72	...
2	38	L : Bacteria	1010	4.24	42.82	33.10
3	27	LN :	1280	4.48	57.31	....
3	39	LN : Bacteria	1450	4.48	64.96	7.65
4	28	LP :	140	2.78	3.89	....
4	40	LP : Bacteria	1440	4.08	58.76	54.87
5	29	LK :	140	3.59	5.03	....
5	41	LK : Bacteria	1010	4.20	42.42	37.39

[1] It is possible, of course, that the inoculated plants might secure somewhat larger supplies of nitrogen from the soil because of their more fully developed root system; but it should still be borne in mind that any such increased root development is due to the inoculation.

Serial No.	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
6	30	LNP :	2280	4.53	103.19	....
6	42	LNP : Bacteria	2780	4.06	112.87	9.32
7	31	LNK :	1570	4.70	73.79	...
7	43	LNK : Bacteria	1890	4.38	82.78	8.99
8	32	LPK :	140	3.15	4.41	....
8	44	LPK : Bacteria	2480	3.82	94.74	90.33
9	33	LNPK :	2300	4.09	94.07	....
9	45	LNPK : Bacteria	3230	4.00	129.20	25.13
10	34	NPK :	2370	4.14	98.12	....
10	46	NPK : Bacteria	2940	4.36	128.18	30.06
11	35	0 :	280	2.63	7.36	....
11	47	0 : Bacteria	730	4.34	31.68	24.32
12	36	0 :	280	2.64	7.39	....
12	48	0 : Bacteria	1020	4.18	42.65	35.26

amounts of nitrogen per acre obtained from the atmosphere by the alfalfa bacteria in the inoculated pots.

Where neither nitrogen nor bacteria were added to the soil, all of the nitrogen removed in the crops[1] must have been derived from the original soil. In the three series of pots receiving no fertilizers (1, 11, and 12) the crops from the uninoculated pots contained 7.31, 7.36, and 7.39 pounds of nitrogen per acre, respectively, while 53.17, 31.68, and 42.65 pounds of nitrogen in the crop are the respective rates per acre of the corresponding inoculated pots. The average of these is 42.50 pounds for the three inoculated pots and 7.35 pounds for the three uninoculated pots, making an average difference of 35.15 pounds in favor of inoculation. In other words, as an average of three separate determinations, with no application of plant food, the bacteria "gathered" and "fixed" and furnished to the growing alfalfa more than 35 pounds of nitrogen per acre. At the present average price for nitrogen in commercial fertilizers (15 cents a pound) these 35 pounds of nitrogen are worth $5.25.

The addition of potassium without phosphorus (5) gave no in-

[1] The amounts of nitrogen given may possibly be too high for some of the uninoculated pots, because of some cross inoculation. The inoculated and uninoculated series of pots stood side by side on the same table, and either spattering of water or more likely the carrying of infected soil by ants (which were frequently found in the pots) or other insects, finally transferred some bacteria to the uninoculated series, which fact became evident, later in the season of 1902, by the development of tubercles, and the markedly increased growth of an occasional plant in the uninoculated pots.

crease in the amount of nitrogen fixed. With phosphorus added to the soil (4), the nitrogen in the crop was increased by the presence of the bacteria from 3.89 pounds to 58.76 pounds per acre, 54.87 pounds of nitrogen per acre having been fixed by the bacteria.

Under the most favorable conditions, when both phosphorus and potassium were applied (8), still more marked results were obtained, the nitrogen in the crop having been increased from 4.41 to 94.74 pounds per acre by the bacteria; that is, the bacteria gathered nitrogen from the air at the rate of more than 90 pounds per acre, which was utilized by the growing alfalfa. At market prices, the nitrogen gathered is worth $13.50 per acre.

It is of interest to observe that even in the pots to which applications of nitrogen had been made (3, 6, 7, 9, 10) some nitrogen was fixed when the soil was inoculated, ranging from 7.65 pounds per acre (3), with no addition of phosphorus or potassium, to 25.13 and 30.06 (9 and 10) pounds per acre under the most favorable conditions, with applications of all mineral elements.

Usually small immature plants contain much higher percentages of nitrogen than do more fully developed plants, but it will be seen from Table IV that, without exception, the heavy crops of alfalfa contained much higher percentages of nitrogen than the lighter crops. Triplicate determinations of nitrogen in the crops from unfertilized pots (1, 11 and 12) showed 2.61 2.63 and 2.64 per cent. of nitrogen in the dry matter from uninoculated pots yielding only 280 pounds of dry matter per acre, and 4.09, 4.34, and 4.18 per cent. of nitrogen in the dry matter from the inoculated pots with an average yield of more than 1,000 pounds per acre. A similar effect was produced in all cases, whether nitrogen was added as a nitrogenous fertilizer or gathered by the bacteria,—all of which tends to prove that, with insufficient nitrogen, the plants make as much growth as possible until the fixation of carbon is practically stopped by the lack of nitrogen, as indicated by the pale yellowish green color of the foliage.

Table V shows the data relating to the fixation of nitrogen from the next cutting (May 21st) of the six unfertilized pots (1, 11, 12), three of which were inoculated.

TABLE V.—FIXATION OF NITROGEN BY ALFALFA IN POT CULTURES; CROPS CUT MAY 21, 1902.

Serial No.	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
I	25	O :	140	2.69	3.77	....
I	37	O : Bacteria	1720	3.52	60.60	56.83
II	35	O :	280	2.47	6.91	....
II	47	O : Bacteria	1170	3.69	43.18	36.27
12	36	O :	280	2.61	7.31	....
12	48	O : Bacteria	1460	3.66	53.48	46.17

These results only confirm those of the previous cutting and show that on ordinary unfertilized Illinois soil the alfalfa bacteria were capable of fixing 46.42 pounds of nitrogen per acre, as the average of the three separate determinations.

The average percentage of nitrogen in the dry matter of the crops from the three uninoculated pots was 2.59, while 3.62 is the average percentage from the three inoculated pots.

Fixation of Nitrogen in Field Experiments.

Table VI gives the same data for the field experiments as are given in Tables IV and V for the pot cultures. These determinations were made on the crops cut from the exact thousandth-acre plots on May 28, 1902.

TABLE VI.—FIXATION OF NITROGEN BY ALFALFA IN FIELD EXPERIMENTS; CROPS CUT MAY 28, 1902.

Plot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
I	O :	1180	1.85	21.81	....
I	O : Bacteria	2300	2.70	62.04	40.23
2	L :	1300	2.02	26.20	....
2	L : Bacteria	2570	2.65	68.02	41.82
3	LP :	1740	2.03	35.40	....
3	LP : Bacteria	3290	2.71	89.05	53.65

These results secured under field conditions on good black prairie soil are in perfect agreement with the results from the pot culture experiments, the amount of atmospheric nitrogen fixed by the alfalfa bacteria being 40.23 pounds per acre on the unfertilized plot, 41.82 pounds on the limed plot, and 53.65 pounds per acre on the plot receiving both lime and phosphorus. Almost two-thirds

of the total nitrogen contained in the crop from the inoculated unfertilized plot (1) was secured from the atmosphere by the alfalfa bacteria. It should be borne in mind that nitrogen is required for root growth as well as for growth above ground and also that these amounts were obtained from a single crop of alfalfa, and that three or four crops will be cut during the season. From the data already given, it will be seen that on the unfertilized soil four such crops as that cut on May 28th from the inoculated plot would mean at least 160 pounds of atmospheric nitrogen fixed by an acre of alfalfa during a single year, and this would require a total yield of only about five tons of alfalfa hay for the season, which is by no means a maximum yield for alfalfa on Illinois soil under the most favorable conditions, as has been shown in the preceding pages.

The percentage of nitrogen is much higher in the crops from the inoculated plots, the average being 1.97 per cent. in the dry matter for the uninoculated plots and 2.69 for the inoculated plots. This means, of course, that the hay produced on the inoculated plots is not only more in quantity, but it is also much better in quality, the percentage of protein averaging only 12.29 in the dry matter of the uninoculated crops, while 16.84 is the average percentage for the inoculated plots.

UNIVERSITY OF ILLINOIS AGRICULTURAL EXPERIMENT STATION.

THE IDENTIFICATION AND COMPOSITION OF MALT LIQUORS.[1]

BY CHARLES LATHROP PARSONS.

Received July 3, 1902.

THREE of our northeastern states have laws which, if enforced, strictly prohibit the sale of all intoxicating liquors and of some which are, perhaps, not intoxicating. In two of these States the statutes use the phrase "Malt Liquors" of any kind, and prosecutions have been brought in large numbers under this section. To obtain convictions, therefore, it has been necessary to convince the judge or jury that the beer in question was brewed

[1] Read at the Pittsburg Meeting of the American Chemical Society.

in part, at least, from malt, for it has quite properly been held in the lower courts that a malt liquor is one which has had germinated grain or some preparation of malt used in its brewing. The question, therefore, submitted to chemists has not been the simple one of alcohol content.

In looking over the literature of the subject almost nothing will be found bearing on this phrase of the question. Much has been written on the essential constitution of pure malt liquors and many analyses have been made to prove that certain beverages were up to standard and that foreign substances had not been used in their preparation. Here, however, it is not to find adulteration but to prove positively that the main source of a first quality beer was used. This would perhaps seem easy from appearance alone but there are beers on the market in these States, with the main physical properties of lager or ale, which analyze quite differently from the pure malt liquors and the representative of at least one of the manufacturers has frequently taken oath that absolutely no malt or preparation of malt was used in their manufacture. The point at issue becomes then very much the same as if the chemist was asked to prove, by analysis, that oleomargarine contained no butter and, if the amounts of malt or butter are small, the solution in either case is, at the present time, equally impossible. The claim has been made that maltose is a characteristic which, if found, would satisfy the meaning of a malt liquor but the contention has naturally met with about as much success as if the presence of butter in oleomargarine was claimed because stearine was present.

If we try to find any one constituent of malt which is absolutely characteristic of that substance and which will be unchanged in the finished beer we immediately encounter difficulties. Diastase, formed in the germinating grain, is destroyed when the beer wort is boiled previous to its fermentation. Maltose and dextrine are large constituents of the glucose which, as the analyses to follow will indicate, and as most brewers admit, is now quite generally used in brewing. Alcohol can arise from sugar of any kind. Sykes,[1] Osborne,[2] Osborne and Campbell,[3] E. Erich,[4] and H.

[1] Transactions Institute of Brewing, **4**, 173 (1891).
[2] *Am. Chem. J.*, **17**, 429, 539 (1895).
[3] *Ibid.*, **18**, 542.
[4] *J. Soc. Chem. Ind.* (1896), p. 366.

Schjerning[1] have given much careful study to the various albuminoses, proteoses, etc., of grain, malt and beer wort but none of these substances appears to persist in an unchanged form in the beer, so that its individual presence could be used as a proof of its source. The bitter principle present has no bearing on the case. The extended investigations of O'Sullivan published in the Journal of the Chemical Society and elsewhere throw no light on this problem. The study of the spectra of the coloring-matter of malt by H. C. Sorby[2] shows it to be characteristic but again it is much modified in beer and, while this field seems worthy of exploration, has not been sufficiently investigated.

Grain and sugar of some form, generally glucose, are the only forms of malt substitutes from which beers are brewed. Of the various sugars used, all have one characteristic in common in that they contain little or no nitrogenous matter or phosphates. Also, while glucose has a considerable and varying amount of ash it is of a distinctly different character from that derived from malt. On the contrary, we have in grain of any kind the essential constituents of malt with the exception of diastase. Fortunately grain can only be used in brewing when mixed with malt in order that the necessary diastase may be furnished. Therefore it may be considered as malt in determining whether or not the beer under examination was a malt liquor. The ash of grain, malted or unmalted, is rich in phosphorus and potassium and poor in sulphates. The ash of glucose is poor in the first-mentioned constituents but is usually rich in sulphates. The nitrogenous matter, the phosphates, which are also characteristic of seed products, and many of the constituents of the ash are conveyed in quite considerable quantities to the beer and give it its chief nutritive value. The beers which are claimed to be brewed mainly from glucose show, on analysis, little nutritive value. This is to be expected if the claims are true. The hops carry some of the above constituents in both cases to the beer. Also I am told by the manufacturer of the only really successful imitation malt liquor on the market, which is claimed to use glucose as its sole source of alcohol, that they are obliged to add some soluble "French albumin" in order to get their yeast to work and that then, although they

[1] *Zischr. anal. Chem.*, **38**, 285 (1896).
[2] *Deut. Viertel. Jahreschrift. offenl. Gesundhtspflg*, II, Heft 1.

boil off part of the alcohol and at the same time Pasteurize the beer, they have great difficulty in preserving it for any great length of time.

The following summary of 172 samples of American lager and 199 samples of American ale, published by Dr. F. E. Englehardt in the Report for the New York Board of Health for 1886 and taken in part from Bulletin 13, part 3, U. S. Department of Agriculture, Division of Chemistry, give a good idea of the average composition of the commercial malt liquors of this country as they were made eighteen years ago.

COMPOSITION OF 172 SAMPLES OF AMERICAN LAGER BEER.

	Sp. gr.	Alcohol by volume.	Extract.	Ash.	Phosphoric acid (P_2O_5).
Average	1.016	4.70	5.86	0.259	0.096
Maximum ..	....	8.78	9.64	0.412	0.120
Minimum ...	....	0.85	3.65	0.172	0.050

COMPOSITION OF 199 SAMPLES OF AMERICAN ALE.

Average	1.013	5.77	5.42	0.307	0.083
Maximum ..	....	11.16	9.50	0.552	0.166
Minimum ...	....	3.02	2.70	0.197	0.0405

Further an average of 28 samples of American malt liquors analyzed by Dr. C. A. Crampton[1] shows the following composition:

COMPOSITION OF 28 SAMPLES OF AMERICAN MALT LIQUORS.

	Sp. gr.	Alcohol by volume.	Extract.	Ash.	Albuminoid ($n \times 6.25$).	Phosphoric acid (P_2O_5).	Reducing sugars as maltose.	Dextrine.
Average ..	1.0161	5.79	5.53	0.279	0.563	0.077	1.65	2.33
Maximum	1.0241	8.63	8.19	0.472	0.763	0.104	2.67	3.12
Minimum.	1.0077	4.85	3.46	0.183	0.400	0.056	0.59	0.90

These analyses are all characterized by notable quantities of albuminoids and phosphates, the lowest amounts being 0.400 and 0.0405 per cent. respectively while the averages are about 0.563 and 0.085 per cent. The larger the quantity of glucose used, the lower, relatively, will be the amounts of nitrogenous and phosphatic material. My own experience leads me to believe that no true lager or ale on the market as such will be found to contain less than 0.04 per cent. of phosphoric acid and 0.25 per cent. of albuminoids, even when these facts are taken into consideration. An amount of glucose equivalent to from 15 per cent. to 20 per

[1] Division of Chemistry, Bulletin 13, Part 3.

cent. of the mashing material appears to be about the maximum quantity used even with the poorest beers derived from malt. König, in his *Menschliche Nahrungs u. Genussmittel,* gives 0.05 per cent. as the minimum amount of phosphoric acid allowable in a beer containing 5 per cent. of extract or over, while the Association of Bavarian chemists[1] gives the minimum amount of albuminoids as 4 per cent. of the extract. It will be seen from the above-quoted analyses and those to follow that their figures are lower than will probably be found in an American malt liquor, even with a considerable proportion of glucose used.

As a further contribution to the literature of this subject I think it will be well to offer the following summary of 76 analyses of beers recently made by me, each of which I considered to give sufficient evidence to warrant a chemist in pronouncing them to have been brewed from malt. This judgment would rest largely upon their percentage of albuminoids and phosphoric acid but is supplemented by the composition in general.

COMPOSITION OF 76 SAMPLES OF AMERICAN MALT LIQUORS.

	Sp. gr.	Alcohol by volume.	Extract.	Albuminoid ($n \times 6.25$).	Phosphoric acid.	Ash.	Sulphates in ash.	Free acid.
Average ..	1.0100	5.61	4.61	0.470	0.061	0.209	6.34	0.26
Maximum	1.0210	7.85	7.64	0.614	0.095	0.296	12.67	0.87
Minimum.	1.0047	0.35	3.15	0.290	0.045	0.147	2.44	0.10

Approximately 50 per cent. of these malt liquors contained salicylic acid.

A glance over this last summary will show at once that the beers analyzed are not equal in quality to those whose analyses have been before quoted. The high percentages of sulphates, the comparatively low specific gravity and extract, point to a much more general use of glucose than formerly existed. This question of quality was also frequently apparent in the physical properties of the beer and it would be a curious thing to know whether or not their sale in so-called prohibition States had anything to do with this quality. In one or two instances only have I any knowledge of the brands.

The average high percentage of free acid shows that some of these beers reached me in anything but the best of condition and the percentages of alcohol were probably modified from the

[1] Bulletin 13, Department of Agriculture, Division of Chemistry, Part 3.

original in many instances. The alcohol is reported in per cent. by volume for the reason that it is the volume per cent. which is usually the legal one. The per cent. of albuminoids and phosphoric acid, is, however, unmodified from that of the perfectly fresh beer for when any yeast was present the container was thoroughly shaken before the sample was taken and the contents of the yeast, which had been derived from the beer, included in the results. It is particularly worthy of note that in some samples not included above, where the alcohol had been wholly changed into acetic acid, the special characters derived from the malt still stood calculated. While the above summary of analyses shows some interesting facts the mistake should not be made of using it as a basis of judging the composition as a whole of fresh American beer and ale. They indicate more closely the kind of material that is apt to be sent to a chemist as the result of a police seizure—material which is sometimes kept several days or even weeks before reaching his hands. If, however, the sample can be treated, when first taken, with eight to ten drops of formaldehyde to the liter of beer, it will keep it in excellent condition, for analytical purposes, for weeks.

If a beer shows the composition given in the analyses already quoted it can safely be pronounced a malt liquor. The converse is not necessarily true. A beer might have had a small amount of malt used in its production and the fact be absolutely undeterminable. In such case, and that is probably just the case with many of the "temperance beers" on the market, chemists can say only "no evidence of malt." The analyst can only be sure of his statements that malt was used when a considerable proportion of that material was used in the brewing. Fortunately the "no malt" beers which have come under my own observation do not even approach the composition of the ordinary part glucose beer.

The following are typical analyses of beer which in my opinion do not furnish sufficient evidence in warranting a chemist in stating that they were brewed from malt.

No.	Sp. gr.	Alcohol by volume.	Extract.	Albuminoid ($n \times 6.25$).	Phosphoric acid.	Ash.	Sulphates.	Free acid.
1	1.0074	1.68	2.52	0.114	0.010	0.19	21.22	normal
2	1.0098	2.63	3.40	0.215	0.023	0.189	....	normal
3	1.0062	2.27	2.25	0.150	0.015	0.124	11.30	normal
4	1.0112	2.11	3.53	0.133	0.015	0.140	10.81	normal
5	1.0041	1.85	1.73	0.031	0.010	0.088	12.50	normal

The percentages of sulphates are high but a glance at the previous table will show at once that too much dependence must not be placed upon this fact. It is simply circumstantial evidence.

The composition of the ash of beers is of great importance in doubtful cases but unfortunately a complete analysis of ash is tedious and would make undesirable expense. Its actual amount tells but little, its composition being the important consideration. Unfortunately, also, more beer is required to obtain enough ash for analysis than is generally sent to the analyst. Blyth[1] gives the following average composition of beer ash:

I have made but one fairly complete ash analysis of any one of the above samples, that of No. 5 of the "no malt" beers, which I place beside that of Blyth's for comparison.

	Malt beer (Blyth).	"No malt" beer (Parsons).
K_2O	37.22	12.93
Na_2O	8.04	19.61
CaO	1.93	undetermined
MgO	5.51	"
Fe_2O_3	trace	"
SO_3	1.44	10.81
P_2O_5	32.09	10.71
Cl	2.91	21.76
SiO_2	10.82	7.50

The differences are very prominent and would be a great help in pronouncing judgment. Here again would arise the same difficulty as before, if only small amounts of malt had been used and the verdict would probably always be in accord with that rendered by the albuminoids and phosphoric acid.

METHODS OF ANALYSIS.

Specific Gravity.—Official method.[1] Pycnometer with thermometer stopper used.

[1] "Foods," Fourth edition, p. 518.

[2] Bulletin No. 65, Department of Agriculture, Bureau of Chemistry.

Alcohol.—Pycnometer with thermometer stopper. Pycnometer carefully calibrated with distilled water at 15.6°, 17°, 20°, and 22° C., according to temperature of atmosphere. Alcohol solution weighed at same temperature. The departure from 15.6° may be criticized but a study of the coefficients of expansion of pure water and mixtures of alcohol and water[1] will show that with such dilute solutions of alcohol as are under consideration the error would be less than 0.01 per cent. This is less than would result from evaporation due to capillarity around the ground-glass stopper if the pycnometer is filled at 15.6° and brought to room temperature to avoid condensation on the glass, is much less than would arise from the use of a hydrometer, even the most delicate made, and is fully as accurate as by calculation from the tables of Squibb. When distinctly acid, the beer was, of course, always neutralized before distillation.

Extract.—Provisional official method,[2] using the formula 1—sp. gr. (of alc. dist.) + sp. gr. (of beer) and using the tables of Oestermann and Schultze. Many comparative results were made by evaporation and by direct determination of the specific gravity of the dealcoholized beer. The results from the use of the tables never varied greatly from the others and are probably much nearer correct owing to the hydrolysis of sugar in the first case and the precipitation of albuminoids, etc., in the second.

Albuminoids (total $n \times 6.25$).—Official Gunning method, with the additional precaution of always first boiling down the beer taken to a small bulk, but not to dryness, after acidification with a few drops of sulphuric acid, before the main quantity of acid or potassium sulphate was added. This did away with the foaming which was otherwise uncontrollable.

Phosphoric Acid.—Uranium acetate method. Solution of uranium acetate in which 1 cc. was equivalent to 0.01 per cent. P_2O_5 when 50 cc. of beer were used. When the beer was light-colored the method was applied both to the beer itself and to the ash; otherwise to the ash alone. The results on the ash were generally 0.1 or 0.2 cc. higher than on the beer itself and sometimes even more when any considerable quantity of yeast had

[1] See Makins: *J. Chem. Soc.*, 99, 224; Silbermann: *Compt. rend.*, October, 1848.
[2] Bulletin No. 65, Bureau of Chemistry.

developed. Results were compared with the molybdate method and agreed closely. There was no difficulty in determining the point of precipitation of the phosphate within 0.1 cc. when the ash was used. The ash was moistened with concentrated hydrochloric acid and the acid evaporated on the water-bath. It was then boiled with 50 cc. of distilled water and titrated with uranium solution. Under these conditions the end-point was always sharp. If the ash was not treated with hydrochloric acid, if acetic acid was substituted for hydrochloric acid or if, after treatment with hydrochloric acid, the ash was heated much above the temperature of boiling water, the phosphates were insoluble or, at least, remained in a form where they were not attacked by the uranium solution. With these precautions, the uranium method gives on a beer ash results which are quite accurate to 0.1 cc., and which are quickly obtained.

Sulphates.—The photometric method of Hinds[1] was used. In my hands his tables give percentages in beer ash more closely agreeing with the gravimetric than when the tables of Jackson[2] were used, as the latter yielded too high results. The solution of ash in hot, dilute hydrochloric acid, was either taken direct after filtering, or the filtered solution from the phosphoric acid determination could be equally well used.

Ash, Salicylic Acid, and Free Acid were determined by the usual official methods.

NEW HAMPSHIRE COLLEGE,
July 2, 1902.

ON AZOXYBENZENE.

Received September 3, 1902.

BY ARTHUR LACHMAN.

A FEW years ago, I endeavored to deduce the structure of the nitro-group, and came to certain conclusions.[3] Subsequent developments, however, showed the line of reasoning then adopted to be erroneous; and these conclusions have since been withdrawn.[4] A new method of investigation became necessary, and a

[1] This Journal, **22**, 269.
[2] *Ibid.*, **23**, 799.
[3] *Am. Chem. J.*, **21**, 433 (1899).
[4] This Journal, **23**, 897 (1901).

study of azoxybenzene, one of the reduction-products of nitrobenzene, seemed to promise useful results. The present paper deals with the properties and the structure of azoxybenzene.

Azoxybenzene stands in a peculiarly intimate and important relation to nitrobenzene. First of all, in its general indifference to all but reducing agents, it closely resembles its mother-substance. Secondly, it still contains oxygen, and has no hydrogen directly attached to its nitrogen atoms. Thirdly, it is always the first, and usually the chief, product of alkaline reducing agents upon nitrobenzene. In view of this important relationship between these two substances, it is curious that so little is known about azoxybenzene. Its natural history is exceedingly meager.

Azoxybenzene was first prepared by Zinin,[1] by the action of alcoholic potash on nitrobenzene. Klinger, at a much later date, investigated the action of different alcohols and alkalies upon aromatic nitro-compounds,[2] and for the preparation of azoxybenzene itself recommended the method still in common use,—reduction of nitrobenzene with a solution of metallic sodium in methyl alcohol. Various other reducing agents have at times been proposed, such as alkaline stannites, sodium amalgam, etc.; but they do not give good yields with nitrobenzene, so far as I have tried them.

The chemical reactions of azoxybenzene have not been exhaustively studied. Mild reducing agents, *e. g.*, metallic iron,[3] remove oxygen, and leave azobenzene; more energetic agents reduce azoxybenzene to aniline, whereby hydrazobenzene[4] often appears as an intermediate product. Aside from these more obvious reactions, only one has attracted more than a passing interest. When azoxybenzene[5] is warmed with concentrated sulphuric acid, it is isomerized to *p*-hydroxyazobenzene:

$$C_6H_5—N_2O—C_6H_5 \rightarrow C_6H_5—N=N—C_6H_4OH.$$

The mechanism of this reaction, which has not yet been satisfactorily explained, will be discussed below.

The data which I have gathered during my study of azoxybenzene are here presented under the following heads:

[1] *J. prakt. Chem.*, **36**, 98 (1845).
[2] *Ber. d. chem. Ges.*, **15**, 865 (1882); **16**, 941 (1883).
[3] Schmidt and Schultz: *Ann. Chem.* (Liebig), **207**, 328 (1881).
[4] *Cf.* Meyer-Jacobson: "Lehrbuch," II, p. 251.
[5] Wallach: *Ber. d. chem. Ges.*, **13**, 525 (1880); **14**, 2617 (1881).

I. The preparation of azoxybenzene.
II. The action of sulphuric acid on azoxybenzene.
III. *p*-Hydroxyazobenzene-*p*-sulphonic acid.
IV. Miscellaneous reactions of azoxybenzene.
V. Some reactions of diphenylnitrosamine.
VI. The constitution of azoxybenzene.

I. THE PREPARATION OF AZOXYBENZENE.

The reduction of nitrobenzene to azoxybenzene is best accomplished by the use of alcohols in alkaline solution. As mentioned above, Zinin used ordinary alcohol and caustic potash. This gives a rather impure azoxybenzene and an imperfect yield. Klinger obtained better results with sodium methylate dissolved in methyl alcohol. The use of metallic sodium in large quantities, however, I found to be inconvenient as well as expensive, for the sodium must be added slowly to the alcohol. A remark of Klinger's, that ordinary methyl alcohol often contains *much water*, suggested the direct use of sodium hydroxide; and it was soon found that a return to Zinin's method, simply changing alkalies and alcohols, gave much the best results.

It was also found, however, that to obtain good yields of azoxybenzene it is essential for the methyl alcohol to be absolutely ketone-free, whereas the amount of water present is relatively without influence. In all the following experiments, the reagents (sodium hydroxide, methyl alcohol, nitrobenzene) were directly mixed, and gently boiled for three hours on a water-bath, a previous test having shown that a separate solution of the alkali before adding nitrobenzene had no influence upon the course of the reaction.

INFLUENCE OF WATER UPON YIELD OF AZOXYBENZENE.

Methyl alcohol acetone-free. cc.	Water. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
800	4	160	120	83
200	8	40	30	75
200	13	40	30	83

In all three cases, the azoxybenzene was of a bright yellow color, and practically pure.

INFLUENCE OF ACETONE UPON YIELD OF AZOXYBENZENE.

Methyl alcohol. cc.	Acetone. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
400	3	80	60	62
650	none	120	100	97
1000	none	200	150	95
650	2.7	120	100	62

In the first and fourth experiments, the azoxybenzene was dark brown, and contained aniline, unaltered nitrobenzene, and isonitrile.

Upon the basis of the above results, the preparation of azoxybenzene is a simple matter. Boil a mixture of 1000 cc. acetone-free methyl alcohol, 200 grams sodium hydroxide and 150 grams nitrobenzene for three hours; distil off the alcohol, and pour the residue into cold water. Freeze the precipitated yellow oil in ice, and wash with water until free from alkali. Then melt the crystals in a little dilute hydrochloric acid to remove traces of aniline, freeze again, and wash free from acid. The resulting crystalline mass is crushed and dried in air, and is now sufficiently pure for nearly all purposes. Azoxybenzene may be recrystallized from alcohol or from ligroin.

SOLUBILITY OF AZOXYBENZENE IN LIGROIN (b. p., 70°-80°).

100 grams ligroin will dissolve at 0° 10.7 grams azoxybenzene.
100 grams ligroin will dissolve at 15° 43.5 grams azoxybenzene.

SOLUBILITY OF AZOXYBENZENE IN ALCOHOL (94 per cent.).

100 grams alcohol will dissolve at 0° 5.0 grams azoxybenzene.
100 grams alcohol will dissolve at 15° 11.4 grams azoxybenzene.

The solubility of azoxybenzene in hot ligroin is so great that when cooled to 0° the solution practically solidifies completely; for purposes of recrystallization it is best to make a saturated solution at the ordinary working temperature and then cool in ice.

II. THE ACTION OF SULPHURIC ACID UPON AZOXYBENZENE.

As mentioned above, Wallach found that hot, concentrated sulphuric acid isomerizes azoxybenzene to *p*-hydroxyazobenzene. Another product of this reaction he found in azobenzene. Wallach's work was confined to the identification of these two substances. In view of the great importance of properly understanding intramolecular rearrangements, I devoted much time to

a study of the mechanism of this reaction, varying the experimental conditions within wide limits.

No intermediate compounds between azoxybenzene and hydroxyazobenzene could be discovered. When azoxybenzene and sulphuric acid are mixed, a dark red solution is formed, with slight evolution of heat. If the mixture is poured into water, azoxybenzene is recovered quantitatively. If allowed to stand in the cold for varying periods of time, the rearrangement proceeds slowly, and is not complete even after a week. If warmed on the water-bath, the reaction proceeds with greater or less velocity, depending upon so many factors that it seems hopeless to find any relationship between them. But in all cases, much the same products are formed in varying amounts, and with more or less unchanged azoxybenzene if the process be interrupted before completion.

Besides the products obtained by Wallach, I have isolated three others. An almost constant product is a black, amorphous powder, insoluble in all ordinary solvents, infusible, difficult to wash, and evidently a high molecular polymerization-product not far removed from free carbon. It contains nitrogen, however. Another product of the reaction is *p*-hydroxyazobenzene-*p*-sulphonic acid. A third product, usually in very small amounts, is an amylamine, probably normal. Its formation is to be explained by an opening of one of the benzene rings in azoxybenzene, with simultaneous oxidation of a carbon atom. Besides these substances, traces of one or more reducing compounds, probably aminophenol and related substances, are usually present; I have not been able to isolate them. Finally, the formation of *o*-hydroxyazobenzene described by Bamberger[1] not long ago could be verified.

These products are formed in amounts depending upon the following factors: the initial temperature of the reaction, the maximum temperature, the concentration of the acid employed, the ratio of sulphuric acid to azoxybenzene, the duration of the experiment, and finally, upon the size and the shape of the containing vessel. The last factor, which may seem captious, finds its explanation in a hitherto unnoticed circumstance; for the reaction of sulphuric acid upon azoxybenzene is strongly exothermic, and may proceed with explosive violence. Ten grams of

[1] *Ber. d. chem. Ges.*, **33**, 3192 (1900).

each substance were warmed on the water-bath; after eleven minutes, the mixture shot out of the flask, with evolution of much sulphur dioxide and oxides of nitrogen, and the formation of voluminous carbon fully twenty times the capacity of the flask. At least three times as much acid as azoxybenzene must be taken to avoid this violent result, as a number of tests showed. Even then, the temperature of the liquid rises above 200°. It is clear that under these circumstances the temperature of the mixture is largely dependent upon the amount of radiation to the outside, which again is a function of the size and shape of the vessel, as well as of the absolute amounts of material taken.

Just what the influence of temperature upon the final result may be, my experiments have not sufficed to determine. As already mentioned, the reaction proceeds slowly even in the cold. On the other hand, I twice carefully warmed a mixture of 10 grams each of sulphuric acid and azoxybenzene (the explosive mixture above) to 85° for ten and for twenty minutes, and recovered 97 and 92 per cent. respectively of unchanged azoxybenzene. The larger the ratio of acid to azoxybenzene, the lower the temperature at which the reaction completes itself; using 200 grams of acid to 10 grams of substance, complete action was obtained at a temperature not exceeding 74°.

It is unnecessary to detail each one of the numerous tests I have made of this reaction; the general conditions that seem to determine the amount of each product will suffice. First a brief account of the method of separation. After warming the mixture for the desired time, it is poured into cold water. Azobenzene, both hydroxyazobenzenes, and the black powder separate. The mixture is shaken out with ether, whereby the powder causes troublesome emulsions; after each extraction, it is best to filter the ether through the same funnel, where the powder finally collects. After being thoroughly washed with ether, the powder must be washed with water to remove sulphuric acid (which it holds tenaciously), and then dried in air. The ether extract is shaken out with dilute alkali to remove hydroxyazobenzene, and then distilled; azobenzene remains, with whatever unchanged azoxybenzene may be recovered. These two substances must be separated by crystallization from alcohol. The alkaline solution

of hydroxyazobenzene is precipitated with an excess of mineral acid, and the compound filtered, washed and dried in air. The original aqueous acid solution contains the sulphonic acid of hydroxyazobenzene, and amylamine. It is rendered alkaline with caustic soda and distilled with steam; the amine passes over very quickly, is collected in hydrochloric acid, and obtained as a salt by evaporation on the water-bath. The residual alkaline solution rapidly darkens in air, and shows reducing action towards ammoniacal silver nitrate, etc. To separate the sulphonic acid, it is rendered slightly acid with sulphuric acid, and boiled down sufficiently to give a saturated solution of sodium sulphate on cooling. The sodium salt of hydroxyazobenzene sulphonic acid separates, being rather insoluble in cold water and still less in sodium sulphate solution.

A. p-Hydroxyazobenzene.—The best yields of hydroxyazobenzene are obtained by using a somewhat diluted sulphuric acid, about 85 per cent. (corresponding to $H_2SO_4 + H_2O$), by taking from five to twenty times as much acid as azoxybenzene, and by keeping the temperature low. From 60 to 75 per cent. of the azoxybenzene may be obtained in its isomeric form. Freed from the ortho-compound as indicated below, and recrystallized from alcohol, it may be obtained in a state of great purity. For the *preparation* of hydroxyazobenzene, the synthetic method of Griess (from diazobenzene and phenol) is much simpler and quicker, as well as less expensive.

B. o-Hydroxyazobenzene.—This compound was first isolated by Bamberger.[1] It is volatile with steam, and can be readily separated from the para compound. From 40 grams mixed *o*- and *p*-hydroxyazobenzene (obtained from 75 grams azoxybenzene in various experiments), I separated 1.5 grams bright red *o*-hydroxyazobenzene (m. p. 81° before recrystallizing). Bamberger registered 190° at the moment of violent action, but as the fluid of the above yield.

C. The Black Powder.—The amount of this amorphous product varies within wide limits—from a trace to 30 per cent. of the azoxybenzene taken. It is formed in greatest amount when the temperature is high and the ratio of acid to azoxybenzene low.

[1] *Loc. cit.*

There is no reason to believe that this substance has a uniform composition. Nothing definite could be learned about it, except that it is in some way related to the formation of amylamine during the rearrangement. Five grams of the powder were heated with 40 cc. concentrated sulphuric acid to 100° for three hours; 0.09 gram amylamine hydrochloride was obtained. In another test, 3.2 grams of powder were heated in a sealed tube with diluted sulphuric acid (1:1): time, three hours; temperature, 220°; yield, 0.35 gram. In a third test, 3 grams were heated almost to fusion with strong caustic soda solution, and the volatile bases collected; 0.30 gram impure salt, giving slight aniline reaction, was obtained.

It seems likely that the powder contains the amylamine group pre-formed, and that the base is detached from the rest of the complex by the action of various agents.

D. Amylamine.—During the first experiments, the amount of amylamine hydrochloride obtained varied from 0.5 to 7 per cent. of the azoxybenzene taken, without affording any clue as to the determining factor. The above experiments with the black powder, and the observation of the high temperature accompanying the rearrangement, suggested the dependence of this product upon the high temperature. A direct trial gave ample confirmation of this view.

Twenty grams azoxybenzene and 45 grams concentrated acid were allowed to heat on the water-bath. An inserted thermometer registered 190° at the moment of violent action, but as the fluid then completely covered the stem, further reading was impossible. Much of the mixture was lost by the explosion, but the collected residues yielded 2.7 grams hydrochloride, a yield of 14 per cent. on the total amount of azoxybenzene.

Amylamine hydrochloride, as obtained by this curious method, forms white needles. It is very soluble in water and in alcohol, but is not deliquescent. With chlorplatinic acid it forms a very insoluble, yellow, prismatic powder, which cannot be recrystallized from water, for it is decomposed, with the separation of metallic platinum, considerably below 100°. Heated in the ordinary melting-point apparatus, it sublimes above 150°; heated quickly on platinum, it can be made to melt, but rapidly volatilizes

under these conditions. It is the salt of a primary base, as shown by the intense isonitrile reaction. For analysis, the salt was recrystallized from water, and dried over sulphuric acid for a few hours.

Analysis:

I. 0.2061 gram gave 20.1 cc. moist nitrogen at 20° and 750 mm.

II. 0.2359 gram gave 0.2712 gram silver chloride.

	Calculated for $C_5H_{11}NH_2.HCl$.	Found.
Nitrogen	11.33	11.13
Chlorine	28.67	28.42
Atomic ratio N : Cl	1 : 1.006	

For lack of time, no experiments were made with the free base, except to note that its boiling-point is about 100°, and that it is quite soluble in water. At some subsequent date, an attempt will be made to study this base, and to work out this somewhat unusual method of preparation. Normal amylamine has been described only by Hofmann,[1] and was evidently obtained by him in very small amount. As prepared above, the base seems to be quite free from ammonia, as well as from secondary or tertiary bases.

E. Hydroxyazobenzene Sulphonic Acid.—The formation of this substance offers no difficulties of explanation; it is a simple case of sulphonation. This is usually a reaction with small velocity; and in this instance, the amount of sulphonic acid produced depends more upon the time during which the substances act upon each other than upon the ratio of acid to azoxybenzene. The maximum yield observed in my experiments was 11 per cent. of the sodium salt (of the weight of azoxybenzene taken). This yield can of course be greatly increased by prolonged heating. A more detailed study of this acid is given below.

F. Azobenzene.—During the energetic rearrangement of azoxybenzene, azobenzene is a constant product. It is formed in amounts varying from 30 to 60 per cent. of the original substance. Being formed in such large quantity, it was by no means clear that it is merely a by-product, as Wallach regarded it; and it was hoped that a careful study of the formation of azobenzene would greatly assist the explanation of how hydroxyazobenzene is formed.

[1] *Ber. d. chem Ges.*, **15**, 770 (1882).

For it is evident that we have three possibilities involved: azobenzene is formed from hydroxyazobenzene; hydroxyazobenzene is formed from azobenzene; or finally, that both are formed simultaneously.

The last possibility, that both are formed at the same time, is ruled out by one experiment. 8.3 grams azoxybenzene stood in the cold for six days, with 35 grams of sulphuric acid of the strength $H_2SO_4 + H_2O$. The products of this reaction were 5.2 grams hydroxyazobenzene and 3 grams unchanged azoxybenzene; mere traces of amylamine and of the sulphonic acid were also observed.

A choice between the first two possibilities was afforded by a direct experiment in which 5 grams of pure hydroxyazobenzene were heated on the water-bath with 20 cc. sulphuric acid ($H_2SO_4 + H_2O$). The products were: Black powder, 0.05 gram; amylamine, unweighable trace of hydrochloride; unchanged hydroxyazobenzene, 3.85 grams; azobenzene, 0.70 gram; sulphonate, 0.45 gram.

It seems clear that the formation of azobenzene is the result of auto-reduction of hydroxyazobenzene; as oxygen is not given off, the black powder is to be regarded as the oxidation product. We have here a case similar to the auto-reduction and auto-oxidation of benzaldehyde under the influence of caustic potash,

$$2\ C_6H_5CHO = C_6H_5CH_2OH + C_6H_5COOH,$$

except that for hydroxyazobenzene the reaction is n-molecular rather than bi-molecular,

$$n\ C_6H_5N{=}NC_6H_4OH = (n{-}x)C_6H_5N{=}NC_6H_5 + [x\ C_6H_5N{=}NC_6H_4OH.(n{-}x)O],$$

where n is a large number, and x a small one.

G. The Mechanism of the Rearrangement.—Further efforts to isolate intermediate products in the rearrangement of azoxybenzene proved futile. Adding acetic anhydride to the sulphuric acid gave results practically the same as above; the products were azo- and hydroxyazobenzene, and the black powder, the amine and the sulphonate being formed only in traces. The direct action of acetic anhydride was also tried; on heating azoxybenzene with it to 200° for five hours, a trace of hydroxyazobenzene was obtained,

but the bulk of azoxybenzene was recovered unchanged (4.8 grams from 5 grams).

A number of explanations have been offered for this rearrangement. Wallach and Belli[1] assume that the first products are phenol, diazobenzene sulphonic acid, and oxygen; and that the former then couple, eliminating sulphuric acid. The oxygen is not accounted for. Friswell and Green[2] similarly assume diazobenzene and phenol as the primary products, which then couple. Other, equally hypothetical explanations are quoted by Beilstein.[3] As I have found hydroxyazobenzene to be formed at temperatures much exceeding 100°, the assumption of a normal diazo reaction in hot sulphuric acid seems somewhat forced. If phenol were formed, its ready sulphonation would lead one to expect at least a small amount of some phenolsulphonic acid in the final product, but such is not the case.

I am inclined to regard the formation of hydroxyazobenzene in this reaction as a direct and immediate intramolecular rearrangement, as are so many other rearrangements of aromatic nitrogen compounds; there is no valid reason for assuming diazobenzene as intermediate. The other products of the reaction, as has been shown above, are secondary in their nature, and can all be obtained from pure hydroxyazobenzene.

It is interesting to note that Zinin, the discoverer of azoxybenzene,[4] tried the action of concentrated sulphuric acid upon this substance, but obtained only unchanged azoxybenzene together with some "gepaarte Schwefelsäureverbindung".

III. *p*-HYDROXYAZOBENZENE-*p*-SULPHONIC ACID.

The sulphonic acid obtained by the action of sulphuric acid upon azoxybenzene was subjected to closer examination, owing to certain discrepancies in the literature. By direct synthesis,[5] the action of diazobenzene-*p*-sulphonic acid upon phenol gives *p*-hydroxyazobenzene-*p*-sulphonic acid,

$$HO_3S—C_6H_4N=N—OH + C_6H_5OH = HO_3S—C_6H_4N=NC_6H_4OH + H_2O.$$

[1] *Ber. d. chem. Ges.*, **13**, 525 (1880).
[2] *J. Chem. Soc.* (London), **47**, 923 (1885).
[3] Third Edition, Vol. IV, p. 1407.
[4] *Loc. cit.*
[5] Griess: *Ber. d. chem. Ges.*, **11**, 2192 (1878).

On the other hand, Wilsing[1] has described a sulphonic acid of the same constitution, but with different properties, which he obtained by the action of sulphuric acid upon azoxybenzene. In undertaking this work, Wilsing was guided by Wallach's recent discovery of the rearrangement to hydroxyazobenzene.

Wilsing's method of preparing his sulphonic acid was to heat azoxybenzene with fuming sulphuric acid (strength not given) to 110° for several hours, until a product completely soluble in water was obtained. In this way, he isolated not only a monosulphonic acid, but also a di-, tri-, and tetra-sulphonic acid. Wilsing himself carefully compared his own mono-sulphonic acid with the synthetic substance, and found many notable points of difference. The most striking difference was met in the action of bromine water; the synthetic product gave a precipitate of tribromphenol, whereas Wilsing's acid was indifferent even at 100°.

On the other hand, the sulphonic acid which I obtained above reacted readily with bromine water as indicated, and was found to be identical in every respect with the synthetic acid. Wilsing's acid cannot possibly have the constitution he assigned to it. In all probability he had azobenzene-sulphonic acid, for the conditions under which he worked (highly concentrated acid) are those which I have found to give chiefly azobenzene as the main product of the rearrangement. The discrepancies in Wilsing's analyses are easily accounted for by the fact that he analyzed the *anhydrous salts* of the acid. I have found the anhydrous salts of these sulphonic acids to be extremely hygroscopic; it is almost impossible to completely dehydrate them by ordinary methods, and the dehydrated salts will gain in weight even in a calcium chloride desiccator; an azobenzene sulphonate containing 1 molecule of water will, of course, give the same analytical results as an anhydrous hydroxyazobenzene sulphonate.

During this comparison I became interested in the manner in which tribromphenol is formed from hydroxyazobenzene sulphonic acid. I used the sodium salt, which was first prepared by Limpricht;[2] it contains 2 molecules of water:

0.7072 gram lost 0.0722 gram at 160°-170°.

[1] *Ann. Chem.* (Liebig), **215**, 228 (1882).
[2] *Ibid.*, **263**, 239 (1890).

	Calculated for $Na.C_{12}H_9N_2SO_4 + 2H_2O$.	Found.
Water	10.7	10.2

The salt requires 140 parts of water at 15° for solution, and crystallizes from hot water in golden yellow, glistening plates of very small size. The anhydrous salt is extremely hygroscopic; two samples, kept in separate calcium chloride desiccators over night, had each gained more than 5 mg.

The sodium sulphonate obtained from azoxybenzene had the same composition, and showed the same solubility.

0.5708 gram lost 0.0574 gram.

	Calculated.	Found.
Water	10.7	10.1

A. The Action of Bromine Water on Hydroxyazobenzene Sulphonic Acid.—When bromine water is added to a solution of this acid (or its sodium salt), a precipitate of tribromphenol is formed instantly. Exactly 6 atoms of bromine are taken up by 1 molecule of the salt. 1.06 grams synthetic sodium salt were titrated with standard bromine water (0.1918 N). When 99.1 cc. had been added, the solution was colorless, and did not smell of bromine; addition of 0.5 cc. bromine water caused a pronounced odor of bromine, which lasted after ten minutes' shaking. One molecule of salt required 6.02 atoms of bromine.

The tribromphenol was filtered and washed: Found, 1.01 grams; calculated, 1.04 grams. The filtrate on evaporation gave the sodium salt of phenolsulphonic acid. (Weighed after drying at 112°). Found, 0.65 gram; calculated, 0.62 gram.

An exactly similar result was obtained with the sulphonate obtained from azoxybenzene: 0.47 gram sodium salt gave 0.48 gram tribromphenol; calculated, 0.47 gram. The filtrate gave 0.29 gram sodium phenolsulphonate; calculated, 0.28 gram.

Finally, the free synthetic sulphonic acid was similarly treated, to make sure that the reaction was not confined to its salts. 0.50 gram sulphonic acid gave 0.56 gram tribromphenol; calculated, 0.59 gram.

The formation of phenolsulphonic acid during this reaction seemed mysterious at first; it was then found to be a secondary product, derived from an *intermediate diazo compound*. The solution, after the addition of bromine water, gives up exactly 1

molecule of diazo nitrogen when boiled (atmosphere of carbon dioxide).

Diazo nitrogen: 0.4579 gram synthetic sodium salt gave 30.7 cc. nitrogen at 13.5° and 741 mm.

	Calculated.	Found.
Nitrogen.....	8.3	7.8

The diazo compound obtained here belongs to the normal, and not to the iso series. In two separate tests, the filtrate from the precipitated tribromphenol was run into alkaline β-naphthol, within less than twenty seconds from the first addition of bromine. In each case, immediate formation of an azo dye was noticed. The solution therefore contained normal diazonium-bromide-*p*-sulphonic acid.

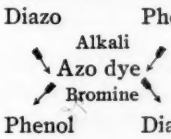
The above analyses permit of a very accurate formulation of the action of bromine upon oxyazobenzene sulphonic acid. The first products are tribromphenol and the diazo compound:

$$HO_3S{-}C_6H_4N{=}NC_6H_4OH + 6Br = C_6H_2Br_3OH + HO_3S{-}C_6H_4N_2Br + 2HBr.$$

The second step consists in the hydrolysis of the diazonium salt:

$$HO_3S{-}C_6H_4N_2Br + H_2O = HO_3S{-}C_6H_4OH + N_2 + HBr.$$

These results are of interest from two points of view. In the first place, we have a reversal of the ordinary coupling reaction of diazo compounds. These react with phenols (in alkaline solution) to form azo dyes; here an azo dye (in acid solution) breaks down into a phenol and a diazo compound:



We have all the typical phenomena of a reversible reaction. This is all the more curious since we usually contrast the stability of azo compounds with the instability of diazo compounds; compare Meyer and Jacobson[1]: "Zünachst ist die grosse Beständigkeit (der Azoverbindungen) hervorzuheben, die im denkbar grössten Gegensatz zu der Unbeständigkeit der Diazoverbindungen steht".

[1] "Lehrbuch," Vol. II, p. 254.

An entirely similar result, for which the explanation is now at hand, was obtained by Witt,[1] who found that chrysoidine (diaminoazobenzene) gives phenol and nitrogen when heated to 150° with dilute hydrochloric acid.

In the second place, the above facts have some bearing upon the theories of Armstrong[2] and of Hewitt.[3] These investigators hold that hydroxyazo compounds possess two *isodynamic* (tautomeric) structures: in alkaline, or it may be neutral solution, or in any medium which fixes the hydroxyl group as such (*e. g.*, glacial acetic acid), we have true hydroxyazo compounds (as formulated above). In acid solution, however, the presence of derivatives of quinonephenylhydrazone is indicated; *e. g.*,

$$HO_3S—C_6H_4NH—N=C_6H_4=O.$$

These authors have attacked the problem experimentally by studying the bromination of the oxygenated benzene ring; a para-substituted phenol is usually brominated in positions 2 and 6; quinone, on the other hand, would *add* bromine first in positions 2 and 3, then in 5 and 6. Thus Hewitt found that hydroxyazobenzene with bromine water gives di-*o*-bromhydroxyazobenzene, and concludes that it is a true hydroxy compound.

The same appears to be true to the hydroxyazobenzene sulphonic acid studied above, in spite of the much greater acidity of its solutions; for it also furnishes a di-*o*-substituted phenol. Another consideration leads to the same result. If we imagine tribromphenol formed from the tautomeric structure given above, the hydrazone molecule would form *iso*-diazobenzene-*p*-sulphonic acid,

$$HO_3S—C_6H_4NH—N=C_6H_4=O \rightarrow HO_3S—C_6H_4NH—NO,$$

whereas we really have a normal diazonium salt produced. We may conclude that there is no reason for assigning to hydroxyazobenzene-*p*-sulphonic acid any other structure than the one indicated by its name.

IV. MISCELLANEOUS REACTIONS OF AZOXYBENZENE.

A. The Action of Hydrochloric Acid upon Azoxybenzene.—Azoxybenzene is quite indifferent towards hydrochloric acid.

[1] *Ber. d. chem. Ges.*, **10**, 656 (1877).
[2] *Proc. Chem. Soc.*, **15**, 243 (1899); **16**, 158 (1900).
[3] *J. Chem. Soc.* (London), **77**, 810 (1900).

Upon heating 1 gram in a current of the dry gas to 100° for two hours, considerable gas seemed to be absorbed; but this escaped on brief exposure to the air, and the azoxybenzene was unchanged in weight and in melting-point.

Similar negative results were obtained upon heating azoxybenzene with concentrated hydrochloric acid solution (sp. gr. 1.20); four hours at 175° produced no change, nor did five hours at 200°. On heating another sample for eight hours to 225°, the azoxybenzene was completely changed, the tube contents were black, much tar was formed, some gas, and the solution gave reactions for phenol, aminophenol, and chlorinated aniline. No hydroxyazobenzene was obtainable. The reaction was not examined further. Werigo[1] has studied the action of hydrobromic acid upon azoxybenzene, and isolated only dibromaniline. From the action of hydriodic acid upon azoxybenzene he obtained some benzidine.

B. The Action of Hydroxylamine upon Azoxybenzene.—Four grams azoxybenzene were boiled with free hydroxylamine and a great excess of potash in methyl alcohol. After six hours, the mixture yielded 3.8 grams unchanged azoxybenzene, and traces of aniline and of azobenzene. Ten grams azoxybenzene were similarly heated in a pressure flask to 100° for sixteen hours. The mixture yielded 8.1 grams azobenzene (90 per cent. of theory), traces of aniline, 0.01 gram *o*-hydroxyazobenzene (m. p. 80°), and 0.02 gram *p*-hydroxyazobenzene (m. p. 150°).

From these experiments it is clear that the action of hydroxylamine upon azoxybenzene is very slow, and consists almost wholly of simple reduction. The formation of the isomeric hydroxyazobenzenes under these conditions is very interesting; but the amounts are very small.

C. The Action of Phenylhydrazine upon Azoxybenzene.—Ten grams azoxybenzene and 5 grams phenylhydrazine were heated to 110° for four hours. Aside from a slight evolution of ammonia, no action could be observed; and all of the azoxybenzene was recovered unaltered.

D. The Action of Zinc Ethyl upon Azoxybenzene.—Two grams azoxybenzene were allowed to stand with 4 grams of zinc ethyl for sixteen days; no action was observable, and all of the azoxyben-

[1] *Ann. Chem.* (Liebig), **163**, 202 (1872).

zene (1.9 grams) was recovered. On heating azoxybenzene with zinc ethyl, a very complex reaction took place. 11.3 grams azoxybenzene were boiled with an excess of zinc ethyl (18 grams) in benzene solution. After one hour, 1000 cc. of gas had been evolved; in another hour, 100 cc. more were collected. This gas contained 27 per cent. ethylene; the balance consisted of ethane. On pouring into dilute sulphuric acid, a basic and a neutral oil were obtained. The basic oil (8 grams) contained aniline and ethyl aniline, and much tar; diethylaniline was carefully sought for, but not found. The neutral oil was directly distilled, and seemed to be thoroughly decomposed during this process. The liquid portion of the distillate seemed to be composed of about equal parts of aniline and ethylaniline. Here again diethylaniline was looked for,[1] but could not be detected. During the distillation, a combustible, basic gas was liberated, probably ethylamine.

No rational equation can be given for the action of zinc ethyl on azoxybenzene. A complex reduction occurs, and the nitrogen atoms seem to be separated. It is possible that in the neutral oil some intermediate product exists, but no suitable method for separating it could be found. This reaction will be the subject of renewed investigation later on.

V. SOME REACTIONS OF DIPHENYLNITROSAMINE.

For reasons to be given further on, it was necessary to subject diphenylnitrosamine to the same reagents used with azoxybenzene. In almost every instance, diphenylnitrosamine gave positive and decisive results under conditions where azoxybenzene gave negative or undecisive ones.

The action of zinc ethyl upon diphenylnitrosamine has already been carefully studied.[2] It will suffice here to summarize the results. When the two substances are brought together, an addition product is formed with almost explosive violence. This addition product, when treated with water, breaks down quantitatively into diphenylamine, diethylhydroxylamine, and zinc hydroxide.

[1] The method of separation employed in this experiment consisted in the use of nitrous acid. The oil was treated with hydrochloric acid and sodium nitrite, after first adding ice and ether. The ethylaniline was immediately extracted as nitrosamine. The residual solution was halved; one part was precipitated with alkaline naphthol, and the azo dye weighed. The other part was distilled with dilute alkali, but gave no diethylamine (from possible nitrosodiethylaniline).

[1] Lachman: *Am. Chem. J.*, **21**, 433 (1899); *Ber. d. chem. Ges.*, **33**, 1022 (1900).

A. The Action of Hydrochloric Acid.—When dry hydrochloric acid gas is allowed to act upon diphenylnitrosamine, even at 0°, nitrosyl chloride is split off. The substance can be readily recognized by its characteristic properties, and when led into potassium iodide solution it liberates iodine and nitric oxide. A quantitative experiment showed that the whole of the nitroso group in diphenylnitrosamine is thus eliminated: 1 gram diphenylnitrosamine (dissolved in ligroin) was treated at 0° with hydrochloric acid gas, and the evolved gases conducted into potassium iodide. Air was carefully excluded by carbon dioxide, as otherwise much iodine is liberated by the catalytic action of nitric oxide. The iodine was titrated with sodium thiosulphate, after first driving out all nitric oxide.

	Calculated	Found.
Iodine	0.641	0.622

The action[1] is represented by the following equation:

$$(C_6H_5)_2N.NO + HCl = (C_6H_5)_2N.H + NOCl.$$

The diphenylamine left after the reaction is not pure, apparently owing to the formation of polymeric products.

B. The Action of Hydroxylamine on Diphenylnitrosamine.—Hydroxylamine and diphenylnitrosamine react in alkaline solution to form diphenylamine and nitrous oxide. Both of these products were obtained quantitatively. Four grams diphenylnitrosamine, 2 grams hydroxylamine hydrochloride, and an excess of methyl alcoholic potash were boiled until the evolution of gas ceased. The gas consisted of nitrous oxide (see below) and contained traces of nitric oxide, as shown by potassium iodide paper. The residual solution was evaporated and extracted with ether and then gave 3.4 grams pure diphenylamine (calculated 3.4 grams). No unchanged nitrosamine was left, for the diphenylamine solution. A direct test showed that less than 0.1 per cent. of nitrosamine in diphenylamine gave a deep blue color under these conditions. One gram nitrosamine was boiled with a slight excess of free hydroxylamine in an atmosphere of carbon dioxide (methyl alcohol solution). 113 cc. moist nitrous oxide were obtained (16° and 737 mm).

[1] See the explanation of this reaction which I have given: *Ber. d. chem. Ges.*, **33**, 1038 (1900).

	Calculated.	Found.
Nitrogen.....	0.22	0.20

In all probability, the first action of hydroxylamine on diphenylnitrosamine results in a normal, oxime-like condensation,

$$(C_6H_5)_2N.NO + H_2NOH = (C_6H_5)_2N.N{=}NOH + H_2O.$$

The intermediate product is unstable (it could not be isolated), and breaks down into nitrous oxide and diphenylamine,

$$(C_6H_5)_2N.N{=}NOH = (C_6H_5)_2NH + N_2O.$$

The reaction proceeds rapidly in the presence of free alkali, requiring not more than fifteen minutes; in the absence of alkali it takes about an hour.

C. The Action of Phenylhydrazine on Diphenylnitrosamine.—When molecular quantities of phenylhydrazine and diphenylnitrosamine are warmed on the water-bath, a violent reaction sets up. Much gas is liberated, and the mixture is shot out of the containing vessel. For the purpose of studying the reaction a little more carefully, two procedures were adopted. The first method consisted in carrying out the operation in sealed tubes. Four grams nitrosamine and 2.2 grams of phenylhydrazine were heated in an evacuated tube. After cooling, 420 cc. gas (corrected) were obtained. This gas was pure nitrogen; its weight is 0.53 gram (calculated for 1 molecule of nitrogen, 0.56 gram). The tube contents gave 3.2 grams diphenylamine, and a little aniline, the amount of the latter being too small to determine. No other products could be found in this or in several other similar experiments; benzene was carefully sought for, but no certain indication of its presence could be obtained.

The second method consisted in boiling the two substances in dry ether for from four to twelve hours. The gas given off under these circumstances contains considerable nitric oxide; if air has access to the flask, a little nitric acid[1] also forms. Nitric oxide also appears in small amount when the substances are heated in a sealed tube still containing air. Here again, no tangible product except diphenylamine could be isolated. From the same quantities as above 3.3 grams diphenylamine were found; calculated 3.4 grams.

[1] This was precipitated during the reaction as phenylhydrazine nitrate, which was analyzed. (Nitrogen found, 24.4 per cent.; calculated, 24.6.)

So far as the two products actually obtained are concerned, the equation may be written as follows:

$$C_6H_5NH—NH_2 + (C_6H_5)_2N.NO = (C_6H_5)_2NH + N_2 + ?(C_6H_5N).$$

It seems, however, that as an actual fact less phenylhydrazine is used up than is called for by this equation; about one-fifth can be recovered as benzalphenylhydrazone after adding benzaldehyde. This interesting reaction will be studied more closely hereafter. In some respects it closely resembles the action of phenylhydrazine on aromatic C-nitroso compounds, recently investigated by Clauser[1]:

$$R—NO + C_6H_5NHNH_2 = R—N< + C_6H_6 + H_2O + N_2.$$

Reference should also be made here to the action of hydrazine (diamide)[2] on diphenylnitrosamine; reduction occurs, diphenylamine and asym.-diphenylhydrazine being the products.

VI. THE CONSTITUTION OF AZOXYBENZENE.

The structure usually assigned to azoxybenzene,

$$C_6H_5—N(\rightarrow O)—N—C_6H_5, \qquad (I)$$

rests upon no direct evidence whatever, and within the last few years a number of authors[3] have suggested the following constitution as an alternative:

$$C_6H_5—N=N(=O)—C_6H_5. \qquad (II)$$

It must be said that as little direct evidence exists for this second structure as for the first. Brühl, to be sure, has found the refractive power of azoxybenzene to be greater than can be accounted for by (I), and even proposes a third structure as equally satisfactory to him:

$$C_6H_5—N\equiv N(\rightarrow O)—C_6H_5. \qquad (III)$$

[1] *Ber. d. chem. Ges.*, **34**, 889 (1901). My own experiments were completed some months before Clauser's paper appeared.

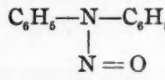
[2] Cited in Beilstein, third edition, Vol. II, p. 339. I was unable to find the author and the journal reference.

[3] Meyer-Jacobson: "Lehrbuch," Vol. II, p. 251 (1894); Bamberger: *Ber. d. chem. Ges.* **29**, 2413 (1896); Brühl: *Ibid.*, **31**, 1361 (1898); **33**, 122 (1900).

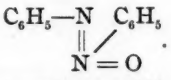
I confess my inability to see any valid differences between (III) and (I); and the present discussion will be confined to formulas (I) and (II). Nor will Brühl's "spectro-chemical" data be considered at this time, for extrapolations of this sort weigh little as *evidence* when applied to wholly unknown atomic groupings.[1]

The general indifference of azoxybenzene to reagents renders it almost impossible to deduce its structure from its own reactions, and for the purposes of the present investigation, a comparative method was chosen. This consisted in the study of the behavior of diphenylnitrosamine towards the same reagents.

There is a very close resemblance between the structure of diphenylnitrosamine and formula (II) above, which is clearly shown by a slightly different method of writing:



Diphenylnitrosamine.



Azoxybenzene (II).

In the first place, the two substances are isomeric; in the second place, each contains two phenyl groups; in the third place, each possesses two nitrogen atoms which are directly joined. Surely, if the similarity extends to the nitrogen-oxygen linking also, some slight similarity of behavior may be looked for in these two compounds.

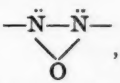
Upon comparing the results reached above, however, we find that no similarity whatever exists. At 0°, diphenylnitrosamine decomposes hydrochloric acid; at 200°, azoxybenzene is unable to do so. At the boiling-point of methyl alcohol, the nitrosamine reacts promptly with hydroxylamine; azoxybenzene is indifferent to it, and is but slowly reduced to azobenzene at a much higher temperature. Diphenylnitrosamine reacts violently with phenylhydrazine; azoxybenzene does not react at all. Diphenylnitrosamine adds zinc ethyl with great energy in the cold; azoxybenzene, on the other hand, does not act at all in the cold, and undergoes complex decomposition when heated with this reagent. Showing no similarity in its reactions to diphenylnitrosamine, azoxybenzene cannot have a similar structure; and nothing remains but to regard the older formula (I) as

[1] See Hantzsch, *Ber. d. chem. Ges.*, **32**, 3148 (1899), for a similar opinion of the applicability of Brühl's data to nitrogen compounds.

the best expression of its chemical behavior; for, after all, the structural formula of a substance is but a condensed account of its chemical behavior.

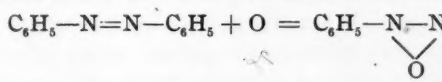
Another line of reasoning also leads to the exclusion of formula (II). Azobenzene, $C_6H_5 - N = N - C_6H_5$, which contains the doubly linked nitrogen atoms assumed in that structure, reacts[1] with zinc ethyl with great violence, yielding ethylene and aniline, (the latter in almost theoretical amount). If azobenzene on the one hand, and diphenylnitrosamine on the other, react so quickly and smoothly with zinc ethyl, the indifference of azoxybenzene points to a marked diversity of structure.

A knowledge of the true structure of azoxybenzene is important from one general point of view: this substance represents the most stable known form of union between oxygen and nitrogen in organic compounds. The azoxy grouping we have just seen to be more inert than the nitroso group; it is more inert than the nitro group. The amine oxides are also much more active than azoxy compounds. If this inertness means anything at all, it indicates that in the grouping,



we have the most complete saturation of the affinities of oxygen and nitrogen for each other.

This is well shown by thermochemical data; azobenzene may be directly oxidized[2] to azobenzene, and the reaction is accompanied by the evolution of considerable heat[3]:



Contrast this with the negative heat of formation of the oxides of nitrogen; for example: nitrous oxide, $2N + O = N_2O - 18oK$; nitric oxide, $N + O = NO - 216K$; $N + 2O = NO_2 - 77K$.

Having thus definitely established the constitution of azoxybenzene, it will perhaps be justifiable to draw the general conclu-

[1] Frankland and Louis: *J. Chem. Soc.* (London), **37**, 560 (1880).

[2] Petriew: Beilstein, Vol. IV, p. 1348. See also the easy oxidation of dinitroazobenzene to the azoxy compound; Werner and Stiasny: *Ber. d. chem. Ges.*, **32**, 3263 (1899).

[3] Petit: *Ann. chim. phys.*, (6), **18**, 160 (1889).

sion that in its nitrogen compounds a bridged oxygen atom shows little tendency towards chemical action, and to apply this conclusion to the study of the valence-problem in other nitrogen-oxygen compounds.

SAN FRANCISCO, August, 1902.

DERIVATIVES OF PHENYLETHER. III.

BY ALFRED N. COOK AND CHARLES F. EBERLY.

Received September 3, 1902.

IN papers[1] previously published, accounts were given of the preparation of several derivatives of phenylether by the action of orthobromnitrobenzene upon ortho-, meta-, and paracresolates of potassium, and by reducing, oxidizing, and sulphonating the resulting compounds. During the past few months the work has been continued and extended to the reaction between the cresols and parabromnitrobenzene with results as given in this paper and two others that will follow.

4-NITRO-2'-METHYL PHENYLETHER, $NO_2.C_6H_4—O—C_6H_4.CH_3$.

This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared by a method described in a previous article).[2] The reaction is represented by the following equation:

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$

Molecular equivalents of the two reacting substances were heated in an oil-bath to 135° C. An action began, as was shown by the agitation of the fused mass, which continued for some time as long as heat was applied. When it was ended the temperature was raised to 160° without inducing any further action. There remained a dark brown liquid and a copious precipitate of potassium bromide. The yield was very good.

The nitro methyl phenylether was separated from the parabromnitrobenzene not acted upon, and other constituents, by fractional distillation under diminished pressure. In a good vacuum it boils about 60° higher than parabromnitrobenzene and much higher than the other contaminating substances.

[1] *Am. Chem. J.*, **24**, 525-529; This Journal, **23**, 806-813.

[2] This Journal, **23**, 806.

4-Nitro-2′-methyl phenylether is a tasteless, oily, reddish brown liquid which is soluble in organic solvents in general. It did not solidify when subjected to a temperature considerably below zero. An attempt to oxidize the side-chain with chromic acid in acetic acid solution was unsuccessful. The phenylether was entirely destroyed. Under a pressure of 27 mm. it boils at 220°-222°. Two analyses for nitrogen gave 6.36 and 6.45 per cent.. Theory requires 6.11 per cent.

4-NITRO-2′-METHYL PHENYLETHER SULPHONIC ACID,
$NO_2.CH_3.C_{12}H_7O.SO_3H$.

This compound was prepared by dissolving the corresponding ether in a small quantity of concentrated sulphuric acid by the aid of the heat of the boiling water-bath. The solution was then diluted with several volumes of water, the excess of sulphuric acid precipitated with lead chloride, and the excess of lead precipitated with hydrogen sulphide. On concentrating the solution to a small bulk a thick, syrupy, red liquid separated out. On redissolving in hot water and allowing to stand, however, it crystallized out in tufts of white needle-like crystals. After recrystallizing several times it melted sharply at 115°. It is soluble in acids, alcohol, and hot benzene, has a bitter taste, and the syrupy liquid previously mentioned has a sharp piercing odor. It also dyes the hands and cloth yellow while the crystalline substance does not do so. A weak, water solution of the acid did not give a precipitate with any of the metals. Its composition was determined by the analysis of the barium salt given below.

Barium Salt, $(CH_3.NO_2.C_{12}H_7O.SO_3)_2Ba$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove all of the sulphuric acid and change all of the free sulphonic acid to the barium salt. It is one of the least soluble salts that have been prepared, on account of which most of it was precipitated with the barium sulphate and had to be extracted from it with hot water, from which it crystallized out in yellow crystalline grains, on cooling. 13.27 parts of the salt are soluble in 1000 parts of hot water at the temperature of the boiling water-bath, and 3.77 parts are soluble in 1000 parts of water at 24° C.

It is therefore approximately twice as soluble as the correspond-

ing salt of 2-nitro-2′-methyl phenylether and about half as soluble as the corresponding strontium salt. Two determinations of the barium after purification by recrystallization from water gave 18.38 and 17.89 per cent. barium. Calculated for $(C_{13}H_{10}O_6NS)_2Ba$, 18.18 per cent.

Copper Salt, $(NO_2.CH_3.C_{12}H_7.SO_3)_2Cu + 5?H_2O$.—The copper salt was prepared by treating a water solution of the barium salt with a molecular equivalent of copper sulphate in water. On concentrating the filtrate a greenish yellow powder was obtained which was desiccated over sulphuric acid. On being heated in the air-bath for some time at 100° it lost in weight and turned brown. On being allowed to come in contact with the air for a few hours it increased in weight and assumed its original color. The results of the determination of the water of crystallization were only fairly satisfactory, but corresponded nearest with 5 molecules.

The Sodium Salt was prepared by treating a water solution of the barium salt with a molecular equivalent of sodium carbonate in water. It crystallized as a fine yellow powder which melted at 233°. It is very soluble in water and the solution is much more yellow than the salt itself.

The Potassium Salt, prepared in an analogous manner with the sodium salt, crystallized from a concentrated water solution in small, yellow flakes which melted at 205°.

4-AMINO-2′-METHYL PHENYLETHER, $CH_3.C_6H_4OC_6H_4.NH_2$.

The free amino compound was prepared from the amino hydrochloride described below by precipitation with ammonium hydroxide. It is soluble in alcohol and benzene, insoluble in ether, and melts at about 60°. Its composition was determined by the analysis of the hydrochloride.

The Amino Hydrochloride was prepared by reducing 4-nitro-2′-methyl phenylether with tin and hydrochloric acid in alcoholic solution while warming on the water-bath. The tin was precipitated with hydrogen sulphide and the filtrate concentrated to crystallization on the water-bath when it assumed a pink tint. It crystallized in long needles and scales, but was recrystallized with difficulty, owing to decomposition. It melted at 182°-183°, and is soluble in alcohol, but insoluble in benzene and ether. Two

analyses of the hydrochloride for chlorine gave 15.15 and 14.88 per cent. Calculated, 15.08 per cent.

The Nitrate was prepared by dissolving the free amino derivative in dilute nitric acid. On cooling, it crystallized in flaky crystals which melted with decomposition at 153°-155°. It is soluble in alcohol and water, but insoluble in organic solvents in general.

The Sulphate, prepared in the same manner as the nitrate, separates from a water solution on cooling in warty crystals. It melts with decomposition at 155°-160°.

The Hydrobromide, prepared in an analogous manner with the two preceding, is soluble in water and alcohol, but insoluble in organic solvents in general. It crystallizes from a water solution in warty aggregations like the sulphate, and melts with decomposition at 200°-204°.

The Platinum Salt was prepared by precipitation from a water solution of the hydrochloride with a solution of chlorplatinic acid. It is a light brown substance which melts with decomposition at 180°-190°. A specimen which had been desiccated over sulphuric acid, when heated in the air-bath at 100°, lost in weight, but increased to its original weight when allowed to remain in contact with the air for some time. Our substance was not of sufficient purity, on account of the difficulty of purifying the hydrochloride from which it was made, to determine the number of molecules of water of crystallization with a high degree of accuracy, but it is probably one.

DINITRO METHYL PHENYLETHER, $(NO_2)_2.CH_3.C_{13}H_7O$.

In the first article on the *"Derivatives of Phenylether"* attention was called to the fact that nitric acid acted on the nitro-methyl derivatives of phenylether, but until the present no attempt was made to study the reaction. On simply mixing the two substances the temperature was slightly raised and the nitric acid assumed a reddish color. On warming, a violent action set in with the evolution of dense brown fumes, the temperature rose to 90°, and the phenylether passed completely into solution. Continued application of heat did not, apparently, cause any further action. The resulting solution was of a deep red color. On diluting with water there was precipitated a yellow oil. On repeated washing

with water and kneading with a glass rod it became viscous and finally solidified, and after repeated crystallization from hot alcohol it melted at 125°.

Nitro-4-nitro-2′-methyl phenylether is a yellow crystalline substance which is soluble in sulphuric ether, petroleum ether, benzene, nitrobenzene and aniline. An attempt to obtain an amino derivative by reducing with tin and hydrochloric acid was unsuccessful, owing to its decomposing when an attempt was made to evaporate the solution to crystallization. The results of the analysis for nitrogen together with its mode of formation, would lead us to the conclusion that it is a dinitro methyl phenylether. Two analyses for nitrogen gave 10.55 and 10.35 per cent. Calculated, 10.22 per cent.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA.
August 10, 1902.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY JOHN V. R. STEHMAN.
Received September 13, 1902.

WALTERS,[1] has shown that ammonium persulphate in the presence of a small amount of silver nitrate can be employed to advantage in place of lead peroxide, for the oxidation of manganese in the colorimetric method.

The writer has been using lead peroxide as an oxidizing agent and titrating the permanganic acid, with a standard solution of sodium arsenite after first filtering free from lead oxides, through an asbestos filter.[2]

In attempting to replace the lead peroxide by the ammonium salt and titrating as before, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

The silver salt can be precipitated by a solution of sodium chlo-

[1] *Age of Steel*, November, 1901; This Journal, **24**, R. 12.
[2] Blair's "Analysis of Iron," third edition.

ride, giving to the solution a fine white background, in which the end-reaction is well marked. It was found necessary with pig irons, to filter free from graphite after solution, as the graphite gives to the solution a peculiar color, in which it was difficult to distinguish the end-reaction.

The following is the method adopted: Weigh off into a 6-inch test-tube 0.2 gram of the sample; add 10 cc. nitric acid (sp. gr. 1.20), heat to boiling in hot water-bath till dissolved, and free from nitrous fumes. Filter into a 10 by 1-inch test-tube (using a small filter), wash filter twice with hot water containing a little nitric acid, and add through the filter to the contents of tube, 15 cc. of a solution of silver nitrate (1.33 grams to the liter). One gram of ammonium persulphate is now added and the solution brought to the boiling-point, using a free flame; heating is continued for about one minute after oxidation begins. The tube and contents are now cooled rapidly under the spigot and poured into a No. 2 beaker, washing out the tube with 30 or 40 cc. of water; 5 cc. of a saturated solution of sodium chloride are now added to the solution in the beaker, silver chloride being precipitated immediately, and titration is begun at once with standard sodium arsenite. The sodium arsenite solution is standardized against standard permanganate or it may be standardized by an iron in which the manganese has been accurately determined. The former is the more rapid and will be found to check closely with the latter.

The ammonium persulphate, as pointed out by Walters,[1] causes complete oxidation only when damp; he therefore adds 10 cc. of water to each pound of the salt the day before used. A determination by the above method may be made in twenty-five minutes in the case of pig irons; with steels, where filtration is not necessary and the sample can be dissolved directly in a large test-tube, the method is more rapid than the color method in which lead peroxide is used as an oxidant.

Below are a few results obtained in pig irons.

[1] *Loc. cit.*

Mn present. Per cent.	Mn found. Per cent.	Mn present. Per cent.	Mn found. Per cent.
0.415	0.423	...	....
0.415	0.414	...	....
0.415	0.414	1.00	0.990
0.415	0.420	1.00	0.989
0.442	0.440	1.00	0.982
0.442	0.460	1.00	0.980
0.442	0.460	1.00	1.010

LABORATORY OF THE E. AND G. BROOKE IRON CO.,
BIRDSBORO, PA.

THE RAPID DETERMINATION OF CARBON BY COMBUSTION.

BY GEORGE AUCHY.

Received September 3, 1902.

SOME experiences with the dry method of combustion having led the writer to the suspicion that the employment of a rapid rate of gas flow is occasionally attended with loss on account of incomplete oxidation by the copper oxide of the products of ignition and combustion, it was thought that it might be advantageous to use the Shimer apparatus with the modification of having the copper oxide in the crucible instead of in a tube.

In this plan the products of combustion are not forced through the copper oxide by the current of oxygen, but are carried in through the apparatus by the current of oxygen *after* oxidation by the copper oxide has been effected. Therefore, the time of contact with the copper oxide is entirely independent of the rate of gas flow employed, and the carbon compounds will be just as thoroughly oxidized by the copper oxide with a fast as with a slow rate. The carbon dioxide is formed and driven to the top of the layer of copper oxide by the heat of the blast-lamp. Is this period of contact with the copper oxide sufficient for complete oxidation? If so, the rapidity of the passage of oxygen is limited only by the capacity of the potash solution to absorb carbon dioxide rapidly and completely. With solution of 1.400 sp. gr. this capacity is very great.

This plan of having the copper oxide in the crucible had been tried by Dr. Shimer himself who in his original article speaks of

an experiment in which the carbon sponge was covered with asbestos coated with copper oxide. The result, however, was a little low. It seemed to the writer to be worth while to do more experimenting in this direction. A new form of large size crucible was used. The one-half-hour-dried carbon residue and asbestos felt of good thickness, which had previously been transferred (without disturbing its shape) from a Hirsch funnel, smallest size, into a small watch-glass for drying, was transferred to the crucible, *carbon side up*[1]; the wad of asbestos used for cleaning out the funnel was placed to one side; both were pressed down evenly on the bottom by a thick glass rod with a spread-out end; the crucible was filled to nearly the point of reaching the inlet tube of the stopper when in position, with finely ground copper oxide freed completely from carbon, and thoroughly tested in this particular by preliminary blank tests; the copper oxide tube was omitted altogether; the blast-lamp was used for ignition, and purified oxygen (air should also serve) was used at a four- or five-bubble rate, allowing ten minutes for the combustion; the oxygen was used throughout, and the potash bulb was weighed filled with oxygen.[2] The following results were obtained:

No.	Regular combustion, 1-bubble rate. Carbon, per cent.	Shimer modified, 4- to 5-bubble rate. 10-minute combustion. Carbon, per cent.
3886	0.85	0.84
3642	0.96 0.95	0.95 0.96
3906 S	1.16	1.145
3819	1.015	1.00
3921	1.13	1.115
3818	1.11	1.12 1.115
3910	1.46 1.46	1.45

[1] After the last washing of the carbon sponge, some of the copper oxide (3 spoonfuls—smallest size horn spoon) diffused in water was poured on and sucked down.

[2] This was proposed by Dr. Dudley who, however, deprecates the use of this plan in important work. In this the writer must disagree with him. But there is a precaution to be observed in this connection. When the bulbs filled with oxygen stand over night they lose weight, probably because of diffusion between the air on the outside and the oxygen within. We have found this loss to be about 0.0030 gram, but it would doubtless vary somewhat in different cases. A correction for this loss must be applied to the first combustion each morning, or, better, the bulbs should be filled with oxygen before use, whenever they stand for some time between successive combustions.

No.	Regular combustion, 1-bubble rate. Carbon, per cent.	Shimer modified, 4 to 5-bubble rate. 10-minute combustion. Carbon, per cent.
3911	0.79	0.795
3868	1.005 0.995	0.99
3954 L 2	1.12	1.105
3952	0.86	0.85
3979 S	0.925	0.19
1.03 S	1.03	1.034
3995	0.90	0.90
3996	0.925	0.92
3697	1.24	1.235
3697 S	1.245	1.245
3685	0.99	0.98
1.08 Std.	1.08	1.086
3929	0.765	0.76
3982	1.06	1.065 1.07
3989 S	1.04	1.025
3991	1.005	0.99
3988 L 2	1.13	1.14

These results, for practical purposes, are very fair indeed. The results are, on the average, 0.007 per cent. low. The doing away with the copper oxide tube is a gain in simplicity.

It was thought that possibly the copper oxide in the crucible, on account of its finely ground condition, might act as an absorbent for the chlorine and hydrochloric acid of the carbonaceous residue. The 1.03 carbon standard was determined with the glass bead tube (the hydrochloric acid absorbent) omitted, result, 1.03 per cent., indicating that all the hydrochloric acid and chlorine is absorbed by the finely ground copper oxide, and that the glass bead tube may therefore also be dispensed with. It would, however, require a considerable number of tests to prove conclusively that all the hydrochloric acid is retained in the crucible in every case. In the meantime, it is some gratification to know that the copper oxide at least helps to absorb it.

In the original Shimer method, the asbestos is placed in the crucible, carbon side down. It might be thought that in using this modification in order to insure a complete combustion, it would be well to make the asbestos layer as thin as possible.

The writer at first, in filtering, covered the asbestos with a layer of the copper oxide, and at the end of the filtration scraped off the

carbon and copper oxide from the asbestos, and placed these in the crucible directly in the bottom and to one side of the asbestos. But in this plan the volatile portion of the carbonaceous residue seems to be driven off before the copper oxide has become sufficiently heated. Results 0.03 per cent. low were obtained in this way in cases of steel which by the process directed above came either right, or only 0.015 low. A good layer of asbestos seems therefore essential, and the writer also makes it a point not to dry thoroughly previous to combustion, but never longer than one-half hour at 90° C. The copper oxide, is, however, thoroughly dried by a short ignition in a platinum dish or crucible before each combustion.

Besides the results given above, there is other evidence which gives the writer confidence in this process. At these works it is the custom to take two samples from each heat of basic open-hearth steel, determining the carbon (and phosphorus) in each.[1] As these two samples may differ in carbon, a close agreement in the results in any one case, proves nothing, with regard to accuracy of method. But many such agreements—one test regular, the other by the Shimer modified—are entitled to be considered as evidence to the accuracy of the latter process. In cases of disagreement and the Shimer result coming low, the latter for a while were repeated by the regular process, and the results of the above table were for the most part obtained in this way.

This plan has now been abandoned on account of risk of getting into "hard" or "soft" spots twice in succession. We now mix together equal weights of drillings from six different samples (pieces of runner) of a heat, and make one combustion.

It is the writer's custom in his daily work to report carbon results in whole numbers or halves, as the case may be, and this custom has been adhered to in this table.

A very great improvement in connection with the carrying out of carbon determinations, and one which once tried will not be abandoned, is Dr. Sargent's plan of rechlorinating the used double

[1] In cases of a greater variation than 0.06 per cent. a third sample (or fourth, if necessary) is taken. The average is taken, not of all the samples, but only of the two whose results agree within 0.06 per cent. The other, or others, are ignored, experiments having indicated that they are merely "hard spots" or "soft spots" as the case may be. Our experience is in agreement with Wahlberg's that low and medium carbon steels are more apt to vary than high carbon steels, and that phosphorus is more likely to vary than carbon.

chloride solution. There is, however, a source of error connected with its use that deserves to be known.

It would seem that solution of drillings should not be accomplished by allowing to stand at rest over night, except a brisk current of air, or brisk stirring by the machine be first used to drive off free chlorine. A current of air, or brisk stirring, will drive off the chlorine before it has time to do any harm to the separated carbon.

LABORATORY OF HENRY DISSTON AND SONS' STEEL WORKS,
PHILA., PA.

NOTES.

Filtration in Determination of Crude Fiber.—All analysts of food products, or feeding-stuffs, are familiar with the difficulty which is often experienced in filtering off the acid and the alkaline extracts in the determination of crude fiber by the official method of the Association of Official Agricultural Chemists. Hence, I wish to suggest the following modification of the usual procedure, which I have found to give very satisfactory results.

Select a funnel of sufficient size to contain the entire bulk of the mixture to be filtered and fit into its point a small platinum filtering cone. Introduce enough ignited asbestos wool to fill the cone a little more than full. Upon moistening, the asbestos wool softens into a fluffy mass which may be drawn down by suction into a close firm filter. The mass to be filtered is now poured into the funnel with the usual care to avoid disturbing the asbestos layer, and suction applied. The filtrate obtained in this manner has always been found to be free of suspended particles of fiber. Filtration is very rapid except when working with finely ground flour, or spices, which tend to clog the filter and impede the flow of the filtrate. In such cases, place the funnel in an ordinary jacket of boiling water or steam, in order to secure hot filtration, transfer the entire mass to be filtered to the funnel and apply suction as usual. The filtration will then proceed at the proper temperature and without further attention from the operator, thus avoiding the two chief objections to the use of the Gooch filter as recommended by the official method. After filtration and washing are completed, transfer the contents of the funnel to a platinum dish,

rinsing the last particles of fiber from the funnel to the dish by means of a fine jet of distilled water. Evaporate off the water thus used, dry to constant weight, and complete the determination as usual.

I prefer this mode of operation to the use of a paper filter, with correction for loss of weight sustained by the paper in a blank determination, as suggested by Winton,[1] for the reason that in addition to the possibility of obtaining additional fiber from the paper used in the acid filtration, I have found that duplicate determinations of the correction to be applied do not always give concordant results, probably because of variations in the weight or composition of individual filters in any given pack of them. Hence, the correction as obtained from a blank determination may not always be a true one and a corresponding error may be introduced in the final computation.

I have used the method outlined above for several years and upon a great variety of samples, with uniformly satisfactory results. In the cases where filtration is slow it proceeds without attention from the analyst, thus relieving the tediousness of the operation very materially. This method of procedure is especially well adapted to the filtration of the glycerol-sulphuric acid mixture used in the König method for determining crude fiber, since in this case hot filtration is imperative.

R. W. THATCHER.

WASHINGTON AGRICULTURAL COLLEGE AND SCHOOL OF SCIENCE,
PULLMAN, WASH., September 18, 1902.

A Rapid Method for Separating Zinc and the Alkaline Metals from Iron.—The separation mentioned by J. W. Rothe[2] has long been used in the determination of aluminum and nickel and I find that it is equally applicable to the separation of zinc, calcium, magnesium, sodium and potassium from large percentages of iron.

Determination of Zinc.

Having the sample (thoroughly oxidized) in solution in the minimum amount of hydrochloric acid (sp. gr. 1.1), transfer to a separatory funnel, add ether and shake well for about eight

[1] Connecticut Agricultural Experiment Station Report, 1898, p. 189; also Bulletin 65, Bureau of Chemistry, U. S. Department of Agriculture, pp. 58, 154, and 155.

[2] Mittheilungen aus den Königlich. Tech. Versuchs-anstalten zu Berlin," 1892, Part III.

minutes. On standing, the lower solution will contain all of the copper and zinc together with a small amount of ferric chloride. Draw off the lower solution, precipitate the copper with hydrogen sulphide, oxidize with a little bromine and precipitate the small amount of iron. The solution is then ready to determine zinc by any approved method. As many zinc ores contain lead, the effect of sulphuric acid was determined. An excess of 3 cc. had no effect on the separation as long as hydrochloric acid was present. In the presence of lead it is better to separate the lead as lead sulphate before making the ether separation, otherwise lead chloride is liable to clog the cock of the separatory funnel. This single separation is very rapid and more effective than a double basic acetate or triple ammonia separation. The separation of the alkaline metals and aluminum from large amounts of iron, as in the complete analysis of iron ores, is made in the same manner as the above. It has the advantage of rapidity and accuracy, and avoids the excessive amount of salts which are always present when basic acetate or ammonia separations are made. H. C. BABBITT.

NEW BOOKS.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY, AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES TO THE END OF 1901. Founded by the Late RICHARD P. ROTHWELL. Edited by JOSEPH STRUTHERS, PH.D. Vol. 10, xxx + 932 pp. New York and London: The Engineering and Mining Journal (Inc.). 1902. Price, $5.00.

This valuable annual publication has appeared since 1892, and is a treasury of information for those interested in the economic side of chemistry and metallurgy. A somewhat extended account of the contents of the present volume would seem, therefore, to be not out of place here.

The total value of the mineral and metal output for 1901 was $1,372,826,102. Among these products pig iron takes the lead, then follow bituminous and anthracite coal, copper, clay products, gold, iron ore, crude petroleum, stone for building, silver, lead, ferromanganese, cement and natural gas in the order named.

It is stated that there has been a falling off in the production of bauxite, but the total consumption was greater than that of 1900. The Pittsburg Reduction Company is erecting a large plant at

Saline County, Arkansas. A large deposit has been discovered in California.

In the manufacture of aluminum the costs are as follows: Energy, 5 cents; alumina, 6 cents; electrodes, 2 cents; chemicals and stores, 1 cent; labor and superintendence, 3 cents; interest and maintenance, 3 cents; total cost, 20 cents. By the use of the Hall process for refining, the cost of alumina is expected to be 2 cents per pound. This saving, with the consequent reduction in price, is a matter of considerable importance and will enable the metal to be sold at a considerable decrease in price. Two noteworthy changes have been made in the corundum industry during 1901. One, the manufacture of an artificial corundum, and the other the development of corundum deposits in Gallatin County, Montana. Cryolite was imported by the Pennsylvania Salt Manufacturing Co. to the extent of 5,383 tons. The value is stated to be $80.00 per ton. The total production of Greenland cryolite was in 1900, 8,960 metric tons.

The sole producer of aluminum in the United States is the Pittsburg Reduction Company, of Niagara Falls, N. Y., and the production for 1901 was 7,150,000 pounds. The metal has been introduced largely in electrical work in place of copper. New works for the production of this material have been established at Shawinigan Falls in Canada. Experience in the use of aluminum as a conductor has shown that it does not resist exposure as well as copper. The metal is now sold at a price of 33 to 37 cents per pound for 99 per cent. metal.

Of the total 523,000 metric tons of ammonium sulphate produced during 1901, 66,000 tons belong to the United States. This is an increase of over 2,000 tons and is mainly accounted for by the increase in the number of by-product coke ovens now operated.

Three hundred short tons of arsenious oxide were made during 1901 by the Puget Sound Reduction Co., Everett, Washington. This is the only producer in the United States. The product is satisfactory in quality and likely to meet the local western demand. It is possible that the producers may be able to have the tariff changed so as to increase the domestic price for arsenic, in which case it may be possible to carry this product around Cape Horn for the New York market at a profit.

An interesting history of the asphalt industry is given by A. W. Dow.

The production of barytes was 49,070 short tons. The use of this material has increased considerably in the manufacture of barium oxide by the Bradley and Jacobs process at Niagara Falls. This increased amount of barium dioxide is used in the manufacture of hydrogen dioxide, and of lithophone.

During the year, the production of crude carborundum was more than doubled, and the consumption for 1902 shows a large estimated increase. This material is to be of considerable importance in the manufacture of window glass in continuous sheets, by a process now being worked out by parties interested in the glass industry.

The production of Portland cement during 1901 has shown a marvelous increase. Foundations for houses, sidewalks, curbs, cement floors for fire-proof buildings, and the like constitute the source of the largely increasing demand. Over 7,000,000 barrels were made in Pennsylvania and nearly 13,000,000 in the United States.

An interesting account of fire-clays and their manufacture into refractory materials is given by Heinrich Ries. A valuable article on the by-product coke industry is contributed by F. Schniewind, and there is an article on gas producers and gas engines by William Kent.

The Neill process for leaching copper ores does not seem to have passed the experimental stage. The chief difficulty connected with its use seems to lie in the fact that the precious metals are not extracted by sulphurous acid. In other respects the process seems to be quite satisfactory.

There is a valuable article on progress in the electrolytic refining of copper by Titus Ulke, and another on the treatment of slimes from the electrolytic refining of copper by Robert L. Whitehead and a very valuable detailed account of the manufacture of blue vitriol by Ottokar Hofmann. Progress in electro-chemistry and metallurgy is covered in a report by John B. C. Kershaw.

There is a valuable, though rather brief article on commercial hydrofluoric acid by Karl F. Stahl, who has installed at Pittsburg

an admirable plant for the production of this very disagreeable and dangerous chemical.

There is a report on progress in gold milling by R. H. Richards and another on the cyanide process by J. S. C. Wells.

The manufacture of artificial graphite at Niagara Falls has increased enormously, 2,500,000 pounds having been produced in 1901 as against 860,000 pounds in 1900. The production of graphitized electrodes especially has shown a very large increase.

During the last few years there has been a marvelous increase in the production of pig iron and steel in the United States. In 1901 there were 16,000,000 tons of pig produced, and of steel over 13,000,000 tons. Of this, nearly 9,000,000 tons were Bessemer and over 4,000,000 open-hearth. The iron ore production was nearly 29,000,000 tons, to which the Minnesota mines contributed over 11,000,000. This year the production from this source seems likely to be very greatly increased.

An article on modern improvement in the manufacture of pig iron by John Birkinbine gives a clear view of the changes in recent practice.

There are articles on white lead manufacture by Parker C. McIlhiney, and recent improvements in lead smelting by H. O. Hofman.

Manganese ores for the production of ferromanganese are obtained from Colorado, Georgia, Virginia, Belgium, Brazil, Canada, Chili, Colombia, Cuba, France, Germany, Greece, India, Italy, Japan, Java, Russia, Sweden, and Spain. There is an article on the Nicopol manganese district in southern Russia by Frank Drake.

The production of natural gas and its use as a fuel and as a source of power in gas engines receives attention in an article by F. H. Oliphant.

Under cyanides from atmospheric nitrogen, allusion is made to the Bradley-Jacobs patent, which consists in coking barium carbonate and small coal. This porous mixture is next converted in the electric furnace into barium carbide. By passing nitrogen gas over this, cyanide is formed.

Rare elements are treated by Victor Lenher, and under the contact process of sulphuric acid, the article by R. Kneitsch, which recently appeared in the *Berichte,* is fully translated.

It would take up too much space to give anything like a full résumé of the contents of this interesting digest of progress. I must content myself with calling attention further to excellent articles on zinc, pyritic smelting, metallography, mine timbering, alloys as solutions, ore dressing, liquefied carbonic acid gas and magnetic separation. The volume ends with a number of statistical tables. EDWARD HART.

INORGANIC CHEMISTRY, WITH THE ELEMENTS OF PHYSICAL AND THEORETICAL CHEMISTRY. By J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York : John Wiley and Sons. 1902. 8vo. viii + 566 pp. Price, $3.00.

The book, as stated in the preface, is intended to supply a rather complete text-book on inorganic chemistry for colleges and universities, and a handy reference book for all students and teachers of chemistry. Opinions should not differ widely as to how well the author has accomplished either of these objects. As far as the former is concerned, the method adopted is almost entirely that of the most objectionable style of dogmatic instruction: laws, hypotheses, definitions are laid down in axiomatic fashion, with scarcely a hint of the broad experimental basis on which they have actually been developed; structural formulas are used from the very beginning with never a word as to the facts which led to their introduction and use; much effort is expended towards making methods of calculation go by rule rather than by reasoning. The reviewer has looked in vain, repeatedly, for the fundamental laws of definite and multiple proportions (!). A discussion of them is promised on p. 57 but diligent search in all but the later chapters of the descriptive part and in the index failed to lead to their discovery!

In a word, not one particle of the beauty of the inductive method, to which chemistry owes its successful development and all its fascination, is left. The student is asked to accept, to believe; his faith and memory are appealed to and cultivated at the expense of his faculty of reasoning and his power of judging at first hand. It is a source of wonder to the reviewer whether any student's interest in chemistry can survive this method of instruction, and how any inherent power of inductive reasoning from fact to hypothesis and law can escape positive destruction. It is con-

ceivable, however, that the method will, unfortunately, find favor in the eyes of some on account of its positiveness and because it is, perhaps, easier to teach dogmatically than to appeal always to the student's judgment and to be prepared with a rational knowledge of facts and their connection to meet convincingly any keen doubter's questions.

The axiomatic statements are not always correct, as, for instance, when it is said on p. 60 that "the atomic weight of an element may be defined as that quantity which combines with one atom of hydrogen"(!) On p. 5 we have the statement that "in gases the molecules repel one another". On p. 61 we have "it has been found that for most substances that can be volatilized without decomposition the vapor density referred to hydrogen is just half the molecular weight"—it would be interesting to know what the exceptions are. Questionable statements are very numerous.

The second object of the book, *viz.*, to serve as a reference book, seems to the reviewer to be more worthy of success than its first object. The descriptive part is good. It includes quite a large number of historical facts and it gives briefly methods of preparation and manufacture for a large number of compounds. The newest important methods are, however, frequently missing. For instance, the absence of any mention of the electric methods of preparing alkalies, chlorates and hypochlorites and of the contact method of manufacturing sulphuric acid is noted. There is a good index.

CHICAGO, October 20, 1902. JULIUS STIEGLITZ.

ACHT VORTRÄGE ÜBER PHYSIKALISCHE CHEMIE. GEHALTEN AUF EINLADUNG DER UNIVERSITÄT CHICAGO, 20. bis 24. Juni, 1901, von J. H. VAN'T HOFF. BRAUNSCHWEIG: F. Vieweg und Sohn, 1902. 15 × 18 cm. 81 pp. Preis: geheftet Mk. 2.50.

These eight lectures, delivered on the occasion of the decennial celebration of the founding of the University of Chicago, are divided into four groups, each consisting of two successive discourses. The subjects treated are the relation of physical chemistry (1) to chemisty, (2) to the industries, (3) to physiology, and (4) to geology. The author considers that the new developments of physical chemistry rest upon the theory of solutions, being essentially an extension of Avogadro's hypothesis to solutions,

and upon the application of thermodynamics, especially of the Carnot-Clausius principle, to chemical problems. The theory of solutions and the dissociation theory of Arrhenius receive consideration in the first and third groups of the lectures, which give a good brief presentation of the theories and what is claimed for them, without, however, even suggesting that there are now many facts known that do not support these hypotheses. Concrete illustrations are given throughout the entire discourses, which are of the character of general outlines. The brief, concise presentation of the author's splendid researches on natural salt deposits is especially interesting and instructive, particularly so because the work was accomplished without the aid of the theory of solutions and the Arrhenius hypothesis. On the part of those readers who do not have an elementary knowledge of physical chemistry, these lectures will require careful study in order to be fully comprehended.

LOUIS KAHLENBERG.

THE CHEMISTRY OF THE TERPENES. By DR. F. HEUSLER, Privat-docent of Chemistry in the University at Bonn. Authorized translation by DR. FRANCIS J. POND, Assistant Professor in the Pennsylvania State College. One vol., 457 pp. Carefully revised, enlarged, and corrected. Philadelphia : P. Blakiston's Son and Co. 1902. Price, $4.00.

The word terpene seems first to have been used by Kekulé. Such words as terebentene, terebene, terpilene, etc., were coined by French chemists to designate the hydrocarbon now known as pinene and its isomers into which it could be converted, *e. g.*, by heat or acids. Some of these terms acquired a generic as well as a specific meaning. The advantage of a word without a double meaning must have been apparent when Kekulé suggested the word terpene, for it soon came into general use.

However, since Baeyer extended the principles of the Geneva Congress nomenclature to the terminology of the terpenes, the word terpene has also acquired a double meaning. On the one hand it is still used in its larger sense comprising all hydrocarbons $C_{10}H_{16}$; on the other, its use has been specialized, restricting it to those hydrocarbons $C_{10}H_{18}$ which are tetrahydro-derivatives of cymene. It is in the former, broader sense in which the term is used in the book before us.

Although substances containing all the way from one to twenty

and possibly more carbon atoms have been found in volatile oils, it is nevertheless remarkable that a large number of volatile plant substances are characterized by ten carbon atoms or a multiple thereof. Whatever significance may attach to this number, this much is true, that the "terpenes and camphors" have always received a larger share of attention than other volatile plant substances.

The secret of this seems to lie in the fact that the terpenes proper and their derivatives occupy places in that enormous field between the series of hydrocarbons and their derivatives belonging to the formula of saturation C_nH_{2n+2} on the one hand and the formula of saturation C_nH_{2n-6} on the other. The study of the terpenes and their derivatives has done fully as much as any one other subject, if not more, to make this vast *terra incognita* of a few decades ago better known. Incidentally these researches have thrown much new light on phyto-chemistry and the manufacture of volatile oils and of perfumes.

The arrangement of the book is that of the German original. The English edition, however, has been made much more valuable by the incorporation of the vast number of facts published since the appearance of Dr. Heusler's monograph. The number of terpenes described is twenty-two, the number of sesquiterpenes, fourteen.

The number of alcohols, ketones, amino derivatives, etc., has increased proportionately. To the same degree to which Dr. Heusler's monograph was indispensable to the investigator five years ago, to the same extent, and even more so, will Dr. Pond's larger work be indispensable to-day. Moreover, it will prove more satisfactory, for the type is larger, the page is better arranged, the references are more handy, and the book is provided with an index. Thus, while Heusler's work was indispensable to the specialist, the English work will prove useful also as a reference work to the non-specialist. EDWARD KREMERS.

HANDBOOK OF TECHNICAL GAS ANALYSIS. BY CLEMENS WINKLER. Translated from the third greatly enlarged German edition by GEORG LUNGE. London : Gurney and Jackson. 1902. 190 pp.

This book is more than the title indicates as it gives Professor Lunge's description of his own apparatus and in many cases his

experience. It deals very fully and satisfactorily with the subjects of the collection and measurement of gases, the preparation of reagents and arrangement of a laboratory.

Two-thirds of the volume is devoted to the apparatus and methods of analysis, almost every important apparatus and method being clearly and minutely explained together with a critique of the various modifications which have been proposed. In many cases a brief historical notice lends interest to the description.

While the references to German periodicals are very complete, the same cannot be said regarding English or American literature, no mention being made of the work of Clowes, of Phillips, of Campbell and Hart and others.

An admirable feature of the work is the attention given to the applications of the methods: it would have seemed better to have included the method of calculation of the losses in chimney gases —a very important subject—than to have referred the student to other books.

Nearly every process is illustrated by examples from practice but it seems somewhat incongruous in a work on *technical* analysis to report the constituents sought to hundredths of a per cent. as is done in nearly every case. Inasmuch as the readings were taken only to tenths of a per cent. and some of the methods are accurate to only half of one per cent., the hundredths must have been obtained arithmetically.

It is, however, a book which should be in the hands of every one having to deal extensively with the analysis of gases.

A. H. GILL.

METHODS OF GAS ANALYSIS. By DR. WALTHER HEMPEL. Translated from the third German edition and considerably enlarged, by L. M. DENNIS. New York: The Macmillan Co. 1902. xix + 490 pp. Price, $2.25.

This well-known book has been very considerably enlarged and improved by Professor Dennis. Not only has the entire work been thoroughly revised and brought up to date but a number of new forms of apparatus and new methods of analysis have been incorporated. The text has been increased by more than one hundred pages. Some of the new methods are: the separation of argon from the atmosphere, the analysis of acetylene, examination

of gases produced by bacteria, new methods for determining carbon monoxide, determination of the heating power of gases, of sulphur in organic substances, the gas lantern, analysis of the gases evolved in the electrolysis of chlorides and in the manufacture of bleaching-powder.

In its new form this work will undoubtedly come to be regarded as the standard text-book and reference book on gas analysis and will be found indispensable in all chemical laboratories.

EDWARD H. KEISER.

SEWAGE WORKS ANALYSES. By GILBERT J. FOWLER, M.Sc. (Vict.) F.I.C. Superintendent and Chemist, Manchester Corporation Sewage Works. New York: John Wiley and Sons. London: P. S. King & Son. 1902. Price, $2.00.

With the development of bacterial processes for the treatment of sewage, has arisen the necessity for constant and careful control of the working of the bacterial filters, and this can only be done by chemical analysis of the effluent. In order to keep a sewage plant in good working condition the effluent from each bed must be constantly examined, and the amount of sewage to be applied to the bed determined by the results thus obtained. The methods that are used for this purpose by Mr. Fowler, manager and chemist of the Manchester Sewage Works, and by Mr. Scudder, of the Mersey and Irwell Commission, are now published for the first time, and the book, "Sewage Works Analyses," is an important addition to the literature of the subject. The methods for determining free, albuminoid, and organic ammonia, nitrogen as nitrites and nitrates, solids in suspension and solution, absorbed oxygen, dissolved oxygen, chlorine, iron compounds, acidity and alkalimetry, are so fully and carefully described, that it would be possible for one who has had very little training in chemistry, not only to understand the methods, but to perform successfully the various determinations. It may, however, be well to call to the attention of those not familiar with sewage analysis, that the English method of determining the oxygen consumed, with potassium permanganate and potassium iodide, is not usually used in this country, but in its place, a modification of Kubel's method, heating a known quantity of the sewage for five minutes with a solution of potassium permanganate, and determining the amount of potassium permanganate used by titrating with oxalic acid;

that of the three methods given for the determination of dissolved oxygen, the indigo method, in the opinion of the writer, though more complicated, gives the best results, and that the colorimetric methods for the determination of ferrous and ferric salts, can only be considered as approximate methods.

Beside the various determinations that have been mentioned the author devotes a chapter of the book to the subject of Chemical Control of Sewage Purification Works, in which he also describes methods for gauging sewage flow, methods of sampling sewage, measuring of sewage sludge, and of determining the degree of purity necessary in an effluent, and in this connection it is to be said that the incubator test, devised by Mr. Scudder and given in detail by Mr. Fowler, is one upon which great importance is now laid, in determining whether or not a sufficient purification of the sewage has been accomplished. The concluding chapter of the book is devoted to the collection and analysis of the gases given off from septic tanks and contact beds, and it is to be regretted that no mention is made of Hempel's methods of gas analysis, which are now so commonly used. Taking the book as a whole, very much can be said in its favor and very little in the way of criticism.

LEONARD P. KINNICUTT.

CONGRÈS INTERNATIONAL D'ÉLECTRICITÉ, PARIS, 1900; par M. E. HOSPITALIER. Paris: Gauthier-Villars. 1901.

This large 8mo. of nearly 500 pages contains the reports and proceedings of the congress. The third section of the congress was devoted to electrochemistry, but the communications on this subject occupy but 22 pages. They include a discussion of the electrochemical nomenclature proposed by Dr. Le Blanc, in which the proposition was generally rejected; a notice of papers by Hollard on the principles of electrolytic analysis and analysis of commercial copper; a short communication of Zenger on the use of sea-salt mother-liquor in a battery cell; a very fragmentary paper by Bouillet on electrochemical deposits; and a paper of 15 pages by Keller on electric furnaces. The above comprises all in the book which touches chemistry, excepting possibly a careful report by G. Claude (23 pp.) on the mechanism of electrolysis by street-railway return-currents. The volume would be out of place in a chemical library, but contains matter of value to the professional electrician.

J. W. RICHARDS.

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